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Spectrometric Identification of Organic Compounds

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Preface

During the past several years, we have been engaged in isolating small amounts of organic compounds from complex mixtures and identifying these compounds spectrometrically.

At the suggestion of Dr. A. J. Castro of San Jose State College, we developed a one unit course entitled "Spectrometric Identification of Organic Compounds," and presented it to a class of graduate students and industrial chemists during the 1962 spring semester. This book has evolved largely from the material gathered for the course and bears the same title as the course.

We should first like to acknowledge the financial support we received from two sources: The Perkin-Elmer Corporation and Stanford Research Institute.

A large debt of gratitude is owed to our colleagues at Stanford Research Institute. We have taken advantage of the generosity of too many of them to list them individually, but we should like to thank Dr. S. A. Fuqua, in particular, for many helpful discussions of NMR spectrometry. We wish to acknowledge also the cooperation, at the management level, of Dr. C. M. Himel, chairman of the Organic Research Department, and Dr. D. M. Coulson, chairman of the Analytical Research Department.

Varian Associates contributed the time and talents of its NMR Applications Laboratory. We are indebted to Mr. N. S. Bhacca, Mr. L. F. Johnson, and Dr. J. N. Shoolery for the NMR spectra and for their generous help with points of interpretation.

The invitation to teach at San Jose State College was extended by Dr. Bert. M. Morris, head of the Department of Chemistry, who kindly arranged the administrative details.

The bulk of the manuscript was read by Dr. R. H. Eastman of Stanford University whose comments were most helpful and are deeply appreciated.

Finally, we want to thank our wives. As a test of a wife's patience, there are few things to compare with an author in the throes of composition. Our wives not only endured, they also encouraged, assisted, and inspired.

Menlo Park, California
April 1963

R. M. Silverstein
G. C. Bassler

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CHAPTER ONE

Introduction

Consider the plight of the chemist confronted with a few milligrams of a completely unknown organic liquid which he has isolated by means of gas chromatography from a complex mixture. Gas chromatography, though fantastically successful as a tool for isolation, affords practically no help in identification, and has the further characteristic of being most effective with small samples.

Let us look at the classical procedures in which the analyst has been trained. First, he smells the liquid. Then he carries out a fusion and qualitative tests for the elements. This is followed by a series of chemical reactions designed to establish a class based on a functional group. Solubility tests, a boiling point, and a refractive index narrow down the possibilities to several in one of the standard tables. A crystalline derivative, whose melting point agrees with the literature and is not depressed by an authentic sample, usually serves for "conclusive" identification. If no satisfactory fit can be obtained, recourse is had to combustion analyses, to a molecular weight determination, and to degradations. It takes a skilled and determined analyst to get by on much less than 20 mg of a compound that has been described in the literature. A good deal more may be necessary for a compound that has not been described. Infrared spectrometry can probably now be considered as a classical tool, and it, of course, saves much chemical

probing to establish functional groups. Actually the classical methodology is an extremely useful device for teaching laboratory skills and organic chemistry per se, and students develop their first "feel" for organic chemistry in the qualitative organic analysis course. Yet, in contrast with methods now available and used in research but *not systematically taught* in universities, the techniques just described are pretty feeble.

This book is written with a single purpose in mind: identification of organic compounds from the responses of the molecule in question to four energy probes. The molecule's responses are recorded as spectra. We are concerned with the following kinds of spectra: mass, infrared, nuclear magnetic resonance, and to a lesser extent, ultraviolet. Our goal in this book will be a rather modest level of sophistication and expertise in each of these areas of spectrometry. Even this level will permit solution of a gratifying number of identification problems. Extension of the methodology from identification of rather simple compounds, about which little or no information is available, to elucidation of structural details of complex molecules, about which quite a bit is known, should be obvious. A higher level of competence in any of the areas of spectrometry is probably best achieved in connection with specific research problems.

In a large number of cases, identification of a completely unknown compound can be made from mass, infrared, and ultraviolet spectra obtained on a tenth of a milligram or less. If a milligram sample is available, the unique data afforded by a nuclear magnetic resonance spectrum can be obtained. These data extend the range of identifications manyfold, and all save the mass spectrometer sample can be recovered.

The orientation throughout the book is on the rationalizations involved in translating spectra into chemical structures. We shall deal only with identification of pure organic compounds. "Pure," in this context, is a relative term, and all we can say is: the purer, the better. Probably the ultimate practical criterion of purity (for a sufficiently volatile compound) is chromatographic homogeneity on two capillary columns (several hundred feet in length), one containing a nonpolar substrate, the other, a polar. Another test is effusion through the micro-leak of a mass spectrometer (see Chapter 2). Various forms of liquid phase chromatography (adsorption and liquid-liquid columns, paper, thin-layer) are applicable to relatively nonvolatile compounds. All of the spectra presented in this book were obtained on samples that were purified by recrystallization to constant melting point, or by gas chromatography.

There is one limitation to the methodology we espouse. A mass spectrum is dependent on a degree of volatility and of thermal stability. And since mass spectrometry is our primary tool, this limitation can be serious. However, mass spectra have been obtained on a large number of high molecular weight compounds—steroids, terpenoids, and alkaloids. Techniques for inserting a sample directly into the ionizing beam of the mass spectrometer promise to loosen further the strictures of volatility and stability.

The problem of cost of necessary instrumentation will be raised, and answered by pointing to the amazing evolution of commercial instruments. The time saved, the smaller sample required, and the information made available far overbalance the cost. Identifications are frequently made on the basis of several hours of a technician's and analyst's time. Under a classical regime, several days or even weeks of a skilled analyst's time would probably be necessary. Infrared and ultraviolet spectrometers have been developed beyond the stage of reliable instruments in the hands of a trained technician. They are now cheap, rugged, and simple enough to be used as a bench tool by the organic chemist. A nuclear magnetic resonance spectrometer is still a fairly expensive, complicated instrument that requires the service of a trained technician. Even here, the recent reduction in cost (by about one-half) and complexity indicates the trend toward use by relatively unskilled personnel backed by a network of factory-trained servicemen. Almost from its inception, the utility of nuclear magnetic resonance spectrometry to the organic chemist has been evident, although its utility in identification in combination with mass, infrared, and ultraviolet spectrometry has not been stressed. Mass spectrometry has had a somewhat different history. Developed by the physicist and utilized extensively by the petroleum chemist, it has been ignored almost completely by the organic chemist concerned with identification and structure determination. Even today there is only a handful of laboratories in which the application of mass spectrometry to these problems is appreciated. And yet, as we shall show, it is undoubtedly the most powerful tool of the four we use. It is still an expensive, complex instrument which requires considerable skill in its use and maintenance. An inexpensive, rugged instrument would find a ready market.

The sequence of spectra chosen would depend on circumstances. If less than a tenth of a milligram is available, infrared and ultraviolet spectra can be run in solution in microcells; the solvent can be removed and a mass spectrum obtained. A volatile sample from which solvent removal is difficult could be handled in an infrared gas cell and transferred directly to the mass spectrometer.

The course given at San Jose State College consisted of 11 hours of lectures and 4 hours of discussion. No laboratory work was involved. The bulk of the course consisted of rationalizations involved in translating spectra into organic structures. Aside from its practical applications, such considerations lead to an appreciation of modern concepts of structural organic chemistry.

We shall spend very little time on instrumentation per se for three reasons: It is not requisite to our goal; we

are not qualified; and excellent treatises are available. The four chapters on spectrometry are designed to give the analyst an appreciation for the potentialities of each technique as applied to the identification of organic compounds. The rest of the book consists of selected spectra. These mass, infrared, nuclear magnetic resonance and ultraviolet spectra are presented as sets, each set representing a compound. These are translated, as exercises, into the chemical structure they represent in twenty cases. Ten sets of spectra are identified only by a Beilstein reference. Ten additional sets are presented without identification.

If we have been judicious in our selection of spectra, they should serve as useful reference material for both teachers and chemists in industry. In one form or another, such material should soon become part of the training of every organic chemist.

CHAPTER TWO

Mass Spectrometry

INTRODUCTION

A mass spectrometer bombards a substance under investigation with an electron beam and records the damage as a spectrum of positive ion fragments and their relative abundance. Separation of the positive ion fragments is on the basis of mass (strictly, mass/charge, but the majority of ions are singly charged). How this is accomplished will be sketched here in just sufficient detail to impart some appreciation to the organic chemist for the potentialities of mass spectrometry as applied to compound identification. The interested reader is referred to the recent general References 1 to 5 at the end of this chapter. J. H. Beynon's monumental book[1] is required reading for anyone seriously concerned with any of the numerous aspects of mass spectrometry.

The first crude mass spectra were produced by Wien[6] in 1898, and by Thomson[7] a few years later. Despite their long history of development, mass spectrometers are hardly commonplace pieces of laboratory equipment. They are still characterized by high cost and the need for highly skilled technicians for operation and maintenance. Despite these characteristics, their routine use in the petroleum industry is well established, and their applications in many other areas are increasing; the organic chemist, in particular, is rapidly becoming aware of their

possibilities. A brief discussion of commercially available instruments has been given by Stewart[2]. In rough figures, an instrument capable of unit resolution (adjacent unit mass peaks are separated by a valley of less than 2% of the height of either peak) up to mass 250 costs about $30,000; usable resolution up to about mass 700 can be had for about $60,000. Very high resolution instruments capable of resolution on the basis of nuclear packing fractions cost over $100,000. The "low cost" instrument should find wide application in identification, particularly of many components separated by gas chromatography. All of our spectra were obtained on an instrument useful to about mass 700 (Model 21–103C, Consolidated Electrodynamics Corporation, Pasadena, California).

A time-of-flight mass spectrometer (The Bendix Corporation, Cincinnati, Division, Cincinnati, Ohio) offers unit resolution to about mass 200 at a cost of about $30,000.

APPARATUS

A schematic diagram of a typical 180° mass spectrometer is shown in Figure 1. There are five component parts:

1. *Sample handling system.* This consists of a device for introducing the sample, a micromanometer for determining the amount of sample introduced, a device (molecular leak) for metering the sample to the ionization chamber, and a pumping system. Introduction of gases is usually a fairly simple matter of transfer from a gas bulb into the metering volume, thence to the inlet sample bottle. Liquids are introduced with various break-off devices, by touching a micropipette to a sintered glass disc or an orifice under mercury or gallium, or simply by hypodermic needle injection through a silicone rubber dam or serum cap. A bulb containing the sample may be pumped out under Dry Ice, then warmed to vaporize the sample into the inlet system. Heated inlet systems are

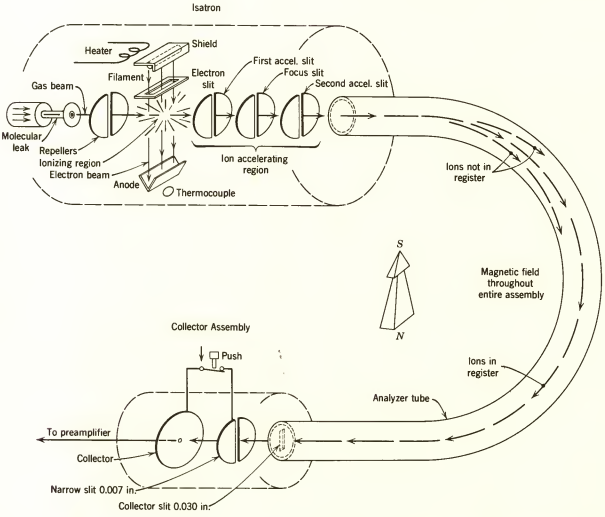


Fig. 1. Schematic diagram of CEC model 21-103 Mass Spectrometer. The magnetic field is perpendicular to the page. (Courtesy of Consolidated Electrodynamics Corporation, Pasadena, Calif.)

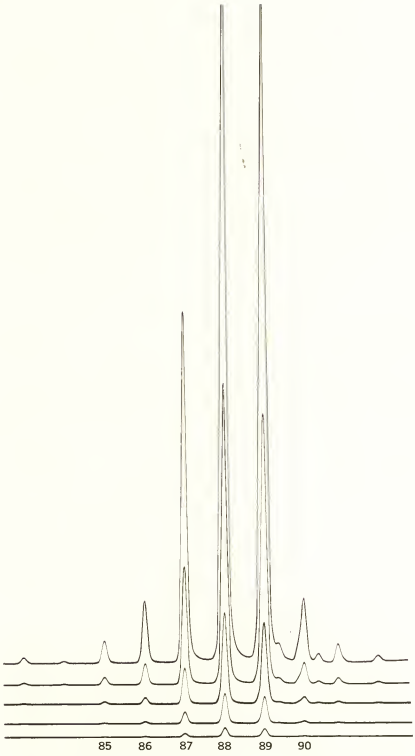


Fig. 2. A portion of a mass spectrum traced by a five-element galvanometer.

used for less volatile liquids and for solids. Insertion of the sample directly into the ionization chamber further extends the limitations imposed by lack of volatility and of thermal stability. Reproducible breakdown patterns have been obtained on high molecular weight terpenoids, steroids, and alkaloids. Even with these special techniques a compound must be stable at a temperature at which its vapor pressure is of the order of 10^{-6} mm. For routine work, a vapor pressure of about 10^{-1} mm–10^{-2} mm is desired. Sample sizes for liquids and solids range from several milligrams to less than 0.1 mg.

2. *Ionization chamber.* The gas stream from the molecular leak enters the ionization chamber (maintained at a pressure of about 10^{-5} mm) in which it is bombarded at right angles by an electron beam emitted from a hot filament. The positive ions, produced by impact of the electron beam, are forced through the first accelerating slit by a small electrostatic field between the repeller electrode and the first accelerating slit. A strong electrostatic field between the first and second accelerating slits accelerates the ions to their final velocities. Additional focusing of the ion beam is provided between the accelerating slits. Ordinarily, the magnetic field applied to the analyzer tube (Figure 1) is held constant, and the accelerating voltage between the first and second ion slits is varied. To obtain a spectrum, the accelerating voltage is decreased at a suitable rate so that the progressively heavier ions are successively brought to the momentum appropriate to the fixed strength magnetic field. Thus, the ions are successively focused at the collector slit as a function of mass (strictly mass/charge). Magnetic scanning is used in some instruments.

3. *Analyzer tube and magnet.* The analyzer tube is an evacuated (10^{-6} mm) curved (in Figure 1, a 180° curve) metal tube through which the ion beam passes from ion source to collector. The magnetic pole pieces (electromagnets are usually used for the larger instruments) are mounted perpendicular to the plane of the diagram (Figure 1). The main requirement is a uniform and highly stable magnetic field.

4. *Ion collector and amplifier.* A typical ion collector consists of one or more collimating slits and a Faraday cylinder; the ion beam impinges axially into the collector, and the signal is amplified by a vacuum-tube electrometer.

5. *Recorder.* A widely used recorder employs five separate galvanometer mirrors which record simultaneously on photographic paper (ultraviolet recording paper, which does not require wet development, is also available). Figure 2 presents a portion of a spectrum traced by a five-element galvanometer system at sensitivity levels decreasing from top to bottom in the ratios of 1:3:10:30:100. Peak heights from the base line are read on the most sensitive trace remaining on scale and are multiplied by the appropriate sensitivity factor.

Another type of instrument is the time-of-flight mass spectrometer. Its name is descriptive. A pulsed electron beam creates positive ions which are accelerated into a field-free region in a straight tube. The velocity of the ion in the free flight path is a function of mass/charge. Its notable characteristic is the speed with which a spectrum is obtained. A commercially available instrument (Type 12 or Type 14, Bendix Aviation Corporation, Cincinnati, Ohio) affords unit resolution to mass 200 and displays up to 10,000 scans per second on an oscillograph. Direct measurement of peak height from the oscillograph is not as accurate as that obtainable from more conventional mass spectrometry, but this can be overcome by counting and recording equipment now available. The rapid response of the time-of-flight instrument permits its direct connection to a gas chromatography unit and analysis of the effluent peaks without necessity of trapping.[8] Figure 3 presents a schematic diagram of a time-of-flight mass spectrometer.

THE MASS SPECTRUM

Introduction

At an electron beam energy of about 9 to 15 electron volts, depending on the molecule involved, a molecular ion (parent ion) is formed by interaction with the beam electrons. In effect, a single electron has been removed from the molecule; the electron beam potential required is called the appearance potential. Recognition of the parent ion (actually a radical ion) is of great importance and worth the effort sometimes involved because it gives the molecular weight of the sample. It should be emphasized at this point that this molecular weight is an exact numerical molecular weight, not the approximation obtained by all other molecular weight procedures familiar to the organic chemist. Mass spectra are usually obtained at an electron beam energy of 70 electron volts, and under these conditions, numerous fragment ions are formed; these constitute the breakdown or fragmentation pattern, and a presentation of the masses of the fragment ions (including the parent ion) versus their relative concentrations constitutes the mass spectrum of the sample. The largest peak in the spectrum, called the "base" peak, is assigned a value of 100%, and the other peaks are reported as percentages of the base peak. In this book, a tabular presentation on this basis will be used. A graphical presentation is also widely used. We prefer the quick grasp of the mass number afforded by a table, to the pictorial impression afforded by a graph. In general, one considers the parent peak, the isotope contributions, the major peaks, and the intervals between these peaks. The parent +1 and the parent +2 peaks (isotope contributions) are given as percentages of the parent peak which is set at 100% in a section following the main part of the table. The parent +4, parent +6

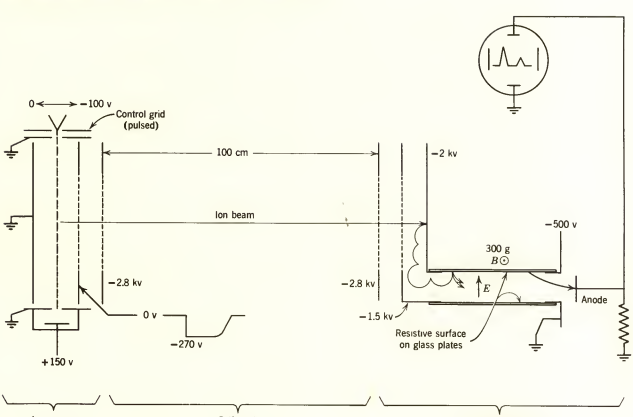


Fig. 3. Schematic of Bendix time-of-flight mass spectrometer.

peaks, and so forth, are given for compounds containing chlorine or bromine.

Authors' Note: We shall use the following notation: ⊙ designates parent radical ion; '+ designates fragment radical ion; and + designates fragment ion.

Fragment Ions

The probability of cleavage of a particular bond is related to the bond strength, to the possibility of low energy transitions, and to the stability of the fragments both charged and uncharged, formed in the fragmentation process. Our knowledge of pyrolytic cleavages can be used, to some extent, to predict likely modes of cleavage of the parent ion. Because of the extremely low vapor pressure in the mass spectrometer (10^{-5} mm), there are very few fragment collisions; we are dealing largely with unimolecular decompositions. This assumption, backed by a file of reference spectra, is the basis for the vast amount of information available from the fragmentation pattern of a molecule. A number of general rules for predicting prominent peaks in a spectrum can be written and rationalized, using concepts of statistics, resonance, hyperconjugation, polarizability, and inductive and steric effects:

1. The relative height of the parent peak is greatest for the straight-chain compound and decreases as the degree of branching increases.
2. The relative height of the parent peak decreases with molecular weight in a homologous series.
3. Cleavage is favored at branched carbon atoms; the more branched, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbonium ion over a secondary, which in turn is more stable than a primary.
4. Double bonds, cyclic structures, and especially aromatic (or heteroaromatic) rings stabilize the parent ion and thus increase the probability of its appearance.
5. Double bonds favor allylic cleavage and give the resonance-stabilized allylic carbonium ion.

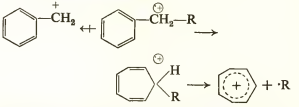
$$CH_2{=}CH{-}\overset{\odot}{C}H_2{-}CH_2{-}R \rightarrow CH_2{=}CH{-}\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2 + \cdot H_2C{-}R$$

6. Saturated rings tend to lose side chains at the α-bond. This is merely a special case of branching (Rule 3).

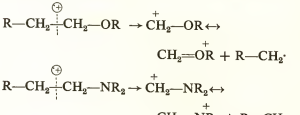
$$\textcircled{s}{-}\overset{\odot}{C}H_2{-}R \rightarrow \overset{+}{\textcircled{s}} + \cdot H_2C{-}R$$

$\textcircled{s}$ designates saturated ring

7. In alkyl-substituted aromatic compounds, cleavage is very probable at the bond beta to the ring giving the resonance-stabilized benzyl ion or, more likely, the tropylium ion directly.



8. Bonds beta to a hetero atom are frequently cleaved, leaving the charge on the fragment containing the hetero atom whose nonbonding electrons provide resonance stabilization.



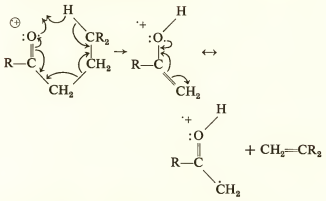
9. Cleavage is often associated with elimination of small stable neutral molecules such as carbon monoxide, olefins, water, ammonia, hydrogen sulfide, hydrogen cyanide, mercaptans, or alcohols. These cleavages often take place with rearrangements and sometimes with the formation of metastable ions which we shall not discuss here (see Reference 1, pp. 251–62).

Mass spectrometry for identification purposes, like other forms of spectrometry, depends heavily on reference spectra. The most extensive catalog of mass spectra (outside of private collections) is that available from the American Petroleum Institute.[9]

Rearrangement Ions

The greatest drawback to structure assignment from a fragmentation pattern is the frequent occurrence of rearrangement ions, sometimes accounting for strong peaks. These are fragments whose origin cannot be described by simple cleavage of bonds in the parent ion, but are a result of intramolecular atomic rearrangement at the moment of fragmentation. Rearrangements involving migration of hydrogen atoms in molecules that contain a hetero atom are especially common. Although rearrangement ions are rarely predicted, their existence can often be rationalized on the basis of low-energy transition pathways and increased stability of the products. Many rearrangement ions, however, defy facile explanation.

A typical example[10] of a common type of rearrangement can be written for a ketone. The arrows represent the movement of single electrons.



The reaction presumably proceeds through a six-membered cyclic intermediate of low activation energy and yields a stabilized radical ion and the stable neutral substituted ethylene molecule.

DETERMINATION OF AN EMPIRICAL FORMULA

In theory, and to some extent in practice, it is possible to arrive at a unique empirical formula with a sufficiently accurate mass measurement alone. For example, it is quite possible, on a very high resolution instrument, to distinguish, at a mass number of 28, among CO, N_2, CH_2N, and C_2H_4. The mass differences between adjacent

Table I

ISOTOPES	% OF ISOTOPE OF LOWEST MASS
C^{13}	1.11
H^2	0.015
O^{18}	0.20
N^{15}	0.37
S^{33}	0.78
S^{34}	4.4
Cl^{37}	32.5
Br^{81}	98.0

combinations are 11.3, 12.6, and 12.6 milli-mass units respectively. These differences result from the fact that each atom differs slightly from its mass number (nearest whole number) by its nuclear packing fraction. We shall not make use of this technique, and the interested reader should refer to the extensive work of Beynon[1]. We shall rely only on the whole mass numbers of the stable isotopes to arrive at several possible empirical formulas and shall select the correct one on the basis of other evidence. We shall restrict ourselves to compounds containing any of the following elements: carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, and iodine. Table I lists the principal stable heavier isotopes of these

elements and their relative abundance as percentages of the isotope of lowest mass.

Our concern then will be with the parent peak (P), the parent + 1 peak ($P + 1$), and the parent + 2 peak ($P + 2$). As Table I shows, important contributions to $P + 1$ are made by C^{13}, H^2, N^{15}, and S^{33}, and to $P + 2$ by O^{18}, S^{34}, Cl^{37}, and Br^{81}. Fluorine and iodine each consist of a single atomic species of mass 19 and 127, respectively; their presence can usually be deduced from the unusual peaks observed in the spectra, and from the small $P + 1$ relative to the molecular weight. If the presence of fluorine is suspected, a fluorine NMR spectrum can be run. Fluorine may also account for otherwise unexplained coupling in a proton NMR spectrum.

Selection of likely empirical formulas appropriate to particular mass and isotope abundance measurements is greatly facilitated by the table constructed by Beynon[1]. A somewhat reduced version of this table is presented as Appendix A. Its use will become more evident as we work through the spectra in this book. In practice, the measured isotope peaks are usually slightly higher than the calculated contributions because of incomplete resolution, because of bimolecular collisions (see below), because of contributions from $P - 1$, or because of impurities. The table is limited to compounds containing C, H, O, and N. The presence of S, Cl, or Br is usually readily apparent because of large isotope contribution to $P + 2$. We shall see that the number of chlorine and bromine atoms can be determined. Apart from mass spectrometry, detection and determination of these elements on minute samples can be conducted by combustion followed by micro coulometric titration;[11] this is particularly useful for monitoring fractions directly as they emerge from a gas chromatographic column.

It is difficult to overemphasize the importance of locating the parent peak. It will be stressed again that this gives an exact numerical molecular weight. Even in cases in which the parent peak is very small, and therefore an accurate determination of $P + 1$ and $P + 2$ is impossible, still only a little extra information can usually lead to identification. This information is available from the source and history of the sample, from the fragmentation pattern and from other spectra. Let us work through the selection of an empirical formula from the isotope abundance data obtained on an organic compound. We are given the following information:

m/e	%
150 (P)	100
151 ($P + 1$)	10.2
152 ($P + 2$)	0.88

The parent peak is mass 150; thus we have the molecular weight. The parent + 2 ($P + 2$) peak obviously does not allow for the presence of sulfur or halogen atoms. We look in the Appendix under mass 150. Our $P + 1$ peak is 10.2% of the parent peak. We list the empirical formulas whose calculated isotope contribution to the $P + 1$ peak falls—to be arbitrary—between 9.0 and 11.0; we also list the calculated $P + 2$ values:

FORMULA	$P + 1$	$P + 2$
$C_7H_{10}N_4$	9.25	0.38
$C_8H_8NO_2$	9.23	0.78
$C_8H_{10}N_2O$	9.61	0.61
$C_8H_{12}N_3$	9.98	0.45
$C_9H_{10}O_2$	9.96	0.84
$C_9H_{12}NO$	10.34	0.68
$C_9H_{14}N_2$	10.71	0.52

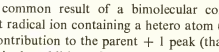
On the basis of the "nitrogen rule" (see below), we immediately eliminate three of these formulas because they contain an odd number of nitrogen atoms. Our $P + 2$ peak is 0.88% of the parent. This best fits $C_9H_{10}O_2$. However, $C_8H_{10}N_2O$ cannot be ruled out without additional evidence.

There are two situations in which identification of the parent peak may be difficult:

1. The parent peak does not appear or is very weak. The obvious remedy in most cases is to run the spectrum at maximum sensitivity (and accept the resulting loss in resolution) and to use a larger sample. (Sometimes a large sample shows up the $P + 1$ peak. See below.) Still the parent peak may not be evident, and other sources of information may be useful. The type of compound may be known, and the parent mass may be deduced from the breakdown pattern. For example, secondary alcohols often give a very weak parent peak, but usually show a pronounced peak resulting from the loss of water ($P - 18$).[12] A molecular weight determination, which can be done on the mass spectrometer (vide infra) or by any of the usual methods, or a combustion analysis, together with consideration of the fragmentation pattern, may help us to arrive at the parent mass. Preparation of a suitable derivative is another device that has been used in a limited way and will probably come to be used more extensively (p. 11). Use of a large sample may sometimes result in the appearance of an anomalous $P + 1$ peak, though the parent peak may still be missing.

2. The parent peak is present but is one of several peaks which may be as prominent or even more prominent. In this situation, the first question is that of purity. If the compound can be assumed to be pure, the usual problem is to distinguish the parent peak from a more prominent parent − 1 peak. One good test is to reduce the energy of the bombarding electron beam to near the appearance potential. This will reduce the intensities of all peaks, but will increase the intensity of the parent peak relative to other peaks, including

fragmentation peaks (but not parent peaks) of impurities. Another test frequently used is to increase the size of the sample, or increase the time the sample spends in the ionization chamber by decreasing the ion repeller voltage.[13] In either case, the net effect is to increase the opportunity for bimolecular collisions to occur. The most common result of a bimolecular collision of a parent radical ion containing a hetero atom (O, N, or S) is a contribution to the parent + 1 peak (that is, the net effect is the addition of a hydrogen atom to the parent radical ion).



parent radical ion parent + 1 ion

Thus, an increase in peak size relative to other peaks, as sample size is increased, or the repeller voltage is decreased, designates that peak as the parent + 1 peak and affords an indirect identification of the parent peak.

Many peaks can be ruled out as possible parent peaks simply on grounds of reasonable structure requirements. The "nitrogen rule" is often helpful in this regard. It states that a molecule of even-numbered molecular weight must contain no nitrogen or an even number of nitrogen atoms; an odd-numbered molecular weight requires an odd number of nitrogen atoms. This rule holds for all compounds containing carbon hydrogen, oxygen, nitrogen, sulfur, and the halogens, as well as many of the less usual atoms such as phosphorus, silicon, arsenic, and the alkaline earths. A useful corollary states that cleavage of a single bond gives an odd-numbered ion fragment from an even-numbered molecular ion, and an even-numbered ion fragment from an odd-numbered molecular ion; the ion fragment must contain all of the nitrogen (if any) of the molecular ion for this corollary to hold. Consideration of the breakdown pattern coupled with other information will also assist in identifying the parent peak.

The presence of appreciable amounts of impurities that give rise to prominent peaks near the parent peak can be troublesome. Here again, the expedient of reducing the energy of the electron beam will cause a relative increase in the intensity of the parent peak (and also of the parent peak of an impurity). The fragmentation pattern will often furnish clues. Another useful technique for detection of impurities is microeffusiometry.[14] A fixed volume of sample is allowed to flow through the molecular leak, and the logarithms of the intensities of the peaks in question are plotted as a function of time. All peaks belonging to the same molecule will give lines of the same slope. Those due to other components of different molecular weight will give lines of different slopes.

Microeffusiometry of the sample also gives an approximate molecular weight.[14] It is also possible to use the inlet system manometer to obtain an accurate pressure of a known volume of vapor, and thus to determine the molecular weight of a weighed sample.

DERIVATIVES

If a compound has low volatility or if the parent mass cannot be determined, it may be possible to prepare a suitable derivative. The derivative selected should provide enhanced volatility, a predictable mode of cleavage, a simplified fragmentation pattern or increased stability of the parent ion. A little work has been done along these lines. The utility of the trimethylsilyl ether derivative of alcohols has been shown.[15,16] These ethers are more volatile than the original alcohol (they should be particularly useful for polyhydric alcohols or phenols), and give a characteristic peak due to cleavage of one of the $Si\text{-}CH_3$ bonds. This $P - 15$ peak may thus be used to calculate the molecular weight of the original alcohol. Methyl esters of high molecular weight monobasic acids or of dibasic acids afford increased volatility and a predictable peak at $P - 31$ (loss of $—OCH_3$).

Reduction of ketones to hydrocarbons[17] has been used to elucidate the carbon skeleton of the ketone molecule. Polypeptides have been reduced with $LiAlH_4$ to give polyamino alcohols, which were volatile and gave predictable fragmentation patterns.[18] Amino acids have been esterified to increase volatility.[19]

MASS SPECTRA OF SOME CHEMICAL CLASSES

Mass spectra of a number of chemical classes are described in terms of the most useful generalizations for identification purposes. For more detail the thorough treatment by Beynon[1] or the references cited should be consulted. A table of common fragments is appended as Appendix B.

Hydrocarbons[9,20–26]

Saturated Hydrocarbons

The great bulk of work in mass spectrometry has been carried out on hydrocarbons of interest to the petroleum industry. Rules 1 to 3 (p. 8) apply quite generally; rearrangement peaks, though common, are not usually intense (random rearrangements[10]); and numerous reference spectra are available.

The parent peak (P) of a straight-chain hydrocarbon is always present, though small for high molecular

weight compounds. The intensity of fragment ions is at a minimum at $P - 15$ since loss of CH_3 from a long straight-chain hydrocarbon is not a likely event (loss of 15 mass units indicates a methyl side chain). The major peaks are characteristically 14 units (CH_2) apart. Peaks at 43 (C_3H_7) and at 57 (C_4H_9) are always large.

A saturated ring in the hydrocarbon increases the relative intensity of the parent peak (Rule 4), and favors cleavage at the bond connecting the ring to the rest of the molecule (α-cleavage, Rule 6). Fragmentation of the ring is usually characterized by loss of two carbon atoms as C_2H_4 (28) and C_2H_5 (29). This tendency to lose even-numbered mass fragments, such as C_2H_4, gives a spectrum that contains a greater proportion of even-numbered mass ions than the spectrum of a straight- or branched-chain hydrocarbon.

Olefins

Correlation of spectra with structure of olefins is more difficult than in the case of saturated hydrocarbons. Rearrangement ion peaks are more common and tend to make the spectra of isomers quite similar. Olefins are generally characterized by the mass-number (C_nH_{2n}) of the parent peak (usually present, Rule 4) and by a series of peaks at 41, 55, 69, 83, 97, and so forth, each two mass units lower than the corresponding peaks (which are also present) of straight-chain saturated compounds. These peaks result from retention of charge on the unsaturated fragment. The base peak usually results from allylic cleavage (Rule 5).

Aralkyl Hydrocarbons

An aromatic ring in a molecule stabilizes the parent peak (Rule 4), which is usually sufficiently large so that accurate measurements can be made on the $P + 1$ and $P + 2$ peaks and an empirical formula obtained. Thus, the initial deduction can be made that the unknown compound may be an aralkyl hydrocarbon. A base peak of 91 ($\overset{+}{C_6H_5CH_2}$) is highly indicative of an alkyl substituted benzene ring. Branching at the α-carbon leads to masses higher than 91 by increments of 14. It is difficult to differentiate between ring position isomers because rearrangements lead to similar spectra; mass 91 frequently appears even in α-disubstituted compounds. A cluster of ions, due to α-cleavage and rearrangement, usually appears at masses 77 (phenyl), 78 (benzene), and 79 (benzene + H). It has been suggested that mass 91, which is common to the spectra of toluene and the xylenes, is a tropylium ion rather than a benzyl ion.[27]

Hydroxy Compounds[9,12,28,29]

Alcohols

The parent peak of alcohols is often quite small, and the expedients already mentioned (pp. 10,11) may be used to identify the parent peak. Frequently the $P - 18$ peak (loss of H_2O) may be mistaken for the parent peak. In fact, the initial elimination of water leads to a spectrum very similar to that of the corresponding olefin.

Cleavage of the bond beta to the oxygen atom is of general occurrence (Rule 8). Thus, primary alcohols show a prominent (frequently the base) peak due to $\overset{+}{C}H_2OH$ (mass 31). Secondary alcohols with a CH_3 on the α-carbon usually have a base peak of mass 45 ($\overset{+}{H}OCHCH_3$). Tertiary alcohols with two CH_3 groups on the α-carbon usually have a base peak of mass 59 ($\overset{+}{H}OC(CH_3)_2$). When more than one C—C bond is beta to the oxygen atom, cleavage of the largest group is favored.

Phenols[9]

A conspicuous parent peak facilitates identification of phenols. In phenol itself, the parent peak is the base peak, and the $P - 1$ peak is small. In cresols, the $P - 1$ peak is larger than the parent peak. A rearrangement peak at mass 77 and prominent peaks from loss of CO and CHO are frequently found in phenols.

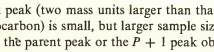
Ethers[9,13]

Aliphatic Ethers

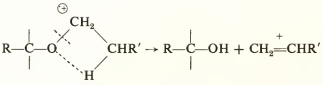
The parent peak (two mass units larger than that of a related hydrocarbon) is small, but larger sample size will usually make the parent peak or the $P + 1$ peak obvious (pp. 10,11). The presence of an oxygen atom is apparent from strong peaks at mass 31, 45, 59, 73, and so forth (RO^+).

Principal peaks are accounted for by the following types of cleavage:

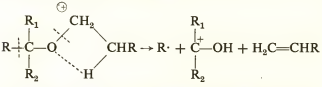
This is β-cleavage (Rule 8), and frequently accounts for the base peak, and for the 45, 59, 73, and so forth, peaks.



This is α-cleavage. The alkyl portion carries the charge and accounts for the 29, 43, 57, 71, and so forth, hydrocarbon peaks.

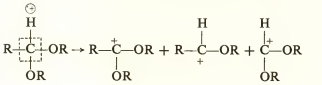


This is α-cleavage with rearrangement. The olefinic fragment carries the charge and gives rise to strong peaks one mass-unit less than those resulting from α-cleavage.



The double cleavage and rearrangement is especially prominent if an alkyl group is α-substituted and neither alkyl group is methyl. This produces the 45, 59, or 73, and so forth, peaks.

Acetals[30] are a special class of ethers. Their mass spectra are characterized by extremely low intensity of the parent ion, and high intensities of the P minus H, P minus R, and P minus OR. Obviously cleavage of any of the bonds of the central carbon atom is facile.



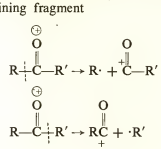
Aromatic Ethers

The parent peak of alphatic ethers of phenols is strong. Cleavage at the β-bond with rearrangement of hydrogen frequently accounts for the base peak. Thus, the base peak of phenetole is 94 ($\phi - \overset{+}{O}H$).

Ketones[9,31]

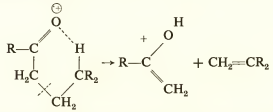
Aliphatic Ketones

The parent peak of ketones is usually quite pronounced. The major fragmentation peaks of aliphatic ketones are those resulting from cleavage at the C—C bonds adjacent to the C=O group, the charge remaining with the oxygen-containing fragment



This cleavage gives rise to mass units of 43, 57, 71, or 85, and so forth. The base peak very often results from loss of the larger alkyl group. Retention of charge on the alkyl fragment gives the same series starting with mass 29.

Cleavage at the second bond from the CO group with rearrangement of a hydrogen atom gives rise to peaks of mass 58, 72, or 86, and so forth, usually of lesser intensity than the odd-numbered peaks from cleavage of the adjacent bond.



The multiple cleavage modes in ketones sometimes make difficult the determination of the carbon-chain configuration. Reduction of the carbonyl group[17] to a methylene group yields the corresponding hydrocarbon whose fragmentation pattern leads to the carbon skeleton.

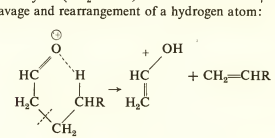
Aromatic Ketones

The parent peak of aromatic ketones is strong. Cleavage of arylalkyl ketones occurs in the β-bond leaving a characteristic $ArC^{+}{=}O$ fragment which usually accounts for the base peak.

Aldehydes[9,32]

Aliphatic Aldehydes

The parent peak and the parent $-$ 1 peak of aldehydes are usually pronounced. For aliphatic straight chain aldehydes higher than propionaldehyde, the base peak is usually 44 ($\overset{+}{C}H_2CHOH$). This results from β-bond cleavage and rearrangement of a hydrogen atom:



Substitution at the α-carbon results in a large peak in the homologous series 58, 72, 86, and so forth.

Other useful peaks for identification are $P - 18$ ($P - H_2O$), $P - 28$ ($P - CO$), and $P - 44$ ($P - CH_2CHOH$). Ejection of a neutral CO fragment from oxygen-containing molecules is quite common. Loss of

the CH_2CHOH fragment results from the β-bond cleavage with the rearrangement depicted, but with the charge remaining on the olefin fragment.

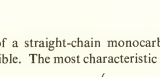
Aromatic Aldehydes

Aromatic aldehydes are characterized by a large parent peak and by a parent $-$ 1 peak which is always large and may be even larger than the parent peak.

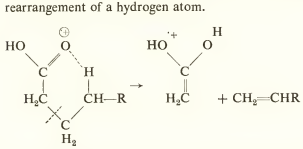
Carboxylic Acids[33,34]

Aliphatic Acids

The parent peak of a straight-chain monocarboxylic acid is usually discernible. The most characteristic (sometimes base) peak is at mass 60



due to cleavage of the bond beta to the C=O group with rearrangement of a hydrogen atom.



The peak at mass 45, due to $COOH^+$ (cleavage of the α-bond), is usually prominent. In the lower molecular weight acids, peaks at $P-17$ (loss of OH), $P-18$ (loss of H_2O), and $P-45$ (loss of COOH) are present. Dibasic acids are usually run as their esters to increase volatility.

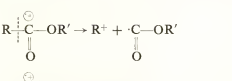
Aromatic Acids[9,34]

The parent peak of aromatic acids is large. The other prominent peaks are formed by loss of OH ($P-17$) and of COOH ($P-45$). Loss of H_2O ($P-18$) is noted if ring hydrogen ortho to the carboxyl group is available. A rearrangement peak ($P-44$) is often present.

Carboxylic Esters[9,35,36]

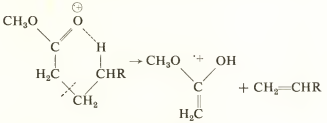
Esters of Aliphatic Acids

The parent peak of an ester of a straight chain monocarboxylic acid is usually discernible. The base peak usually results from one of the following types of cleavage.



Both R^+ and $RC^+{=}O$ form the characteristic "paraffin" peaks (29, 43, 57, or 71, and so forth). A prominent peak at 59, 73, 87, and so forth, is formed by cleavage at the bond alpha to the C=O group, the charge remaining on the oxygen-containing fragment

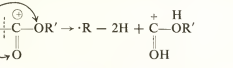
Mass 74 is frequently the base peak of methyl esters of higher fatty acids.[36] It arises, as does mass 60 from fatty acids, from cleavage of the bond beta to the C=O group with rearrangement of a hydrogen atom.



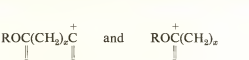
Mass 88 is prominent in ethyl esters of fatty acids and arises in the same way. Branching at the α-carbon gives rise to the higher members of the homologous series starting with 74 (88, 102, 116, and so forth).

When R is heavier than propyl, the olefinic rearrangement ions ($R-1$) become noticeable, and sometimes quite prominent (42, 56, 70, 84, 98, and so forth).

Other diagnostically useful but smaller peaks (61, 75, 89, 103, and so forth) result from elimination of R and transfer of two hydrogen atoms to the oxygen containing fragment.



Esters of dibasic acids, $ROC(CH_2)_xCOR$, in general, give recognizable parent peaks. Intense peaks are found at

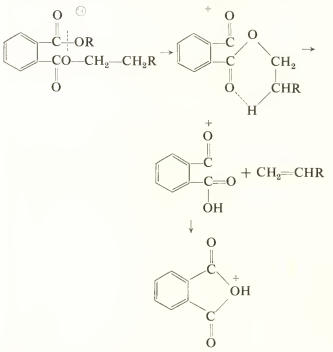


Esters of Aromatic Acids

The parent peak of aromatic esters is prominent. The base peak of methyl esters of mono- and polybasic carboxylic esters is ($P - 31$) corresponding to loss of OCH_3. Cleavage of $COOCH_3$ from the ring furnishes another strong peak ($P - 59$).

As the alkyl group increases in length, the modes of cleavage begin to resemble those obtained from aliphatic esters: cleavage of OR accompanied by rearrangement of one or two hydrogen atoms, and cleavage of the alkyl group to give a peak corresponding to R^+.

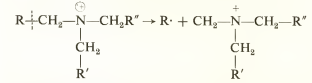
A strong characteristic peak at mass 149 is found for all esters of phthalic acid higher than the dimethyl ester. Apparently this is formed by the following sequence:



Amines and Amides[9,37]

Aliphatic Amines

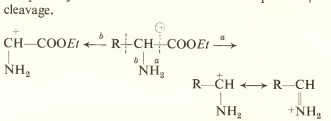
The parent peak of an aliphatic monoamine is an odd number but is often quite weak. The base peak usually results from cleavage of the bond beta to the N atom (Rule 8); for primary amines unbranched at the α-C atom, this is mass 30. Prominent peaks, therefore, appear in all amines at 30, 44, 58, 72, 86, or 100, and so forth. Cleavage of the longer chain is generally preferred:



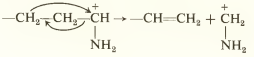
A large peak at 30, however, does not necessarily indicate a primary amine; double cleavage and rearrangement of a hydrogen atom in secondary and tertiary amines frequently lead to an appreciable peak at 30.

Supporting evidence for an amine structure can usually be obtained by noting the prominent NH_3^+ ion at mass 18. This can be distinguished from the H_2O^+ ion by the ratio of the mass of 18 to that of 17; the ratio is generally much greater for amines than for water.

Mass spectrometry of ethyl esters of amino acids has recently been reported.[19] The most common mode of cleavage was loss of the $COOEt$ group (cleavage *a*), the charge remaining on the nitrogen containing fragment. Cleavage *b* also occurred, giving a moderate peak at 102 for primary amino acids. Both modes represent β-cleavage.



Olefin elimination from the amine fragment gave a moderate peak at mass 30 in most cases.

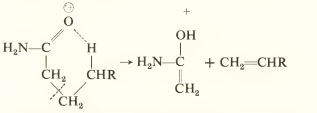


Aromatic Amines

The parent peak (odd number) of aromatic amines is large. Fragmentation of the ring of aniline itself occurs with loss of HCN and H_2CN to give peaks of mass 66 and 65. This is analogous to loss of CO and HCO from phenol. Alkyl groups, attached to the ring of aniline, cleave preferentially at the β-bond.

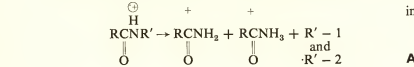
Aliphatic Amides

The parent peak (odd number) of straight-chain monoamides is usually discernible. The characteristic (the base peak in primary straight-chain amides higher than propionamide) peak is mass 59. This results from cleavage of the bond beta to the C=O group and rearrangement (similar to acids).



Cleavage of long-chain primary amides also occurs at the γ-bond without rearrangement to give mass 72, and with rearrangement to give mass 73.

Secondary and tertiary amides give similar rearrangement peaks. Cleavage of the N-alkyl group also occurs with rearrangement of one or two hydrogen atoms.



Aliphatic Nitriles[9,39]

The parent peak (odd number) of aliphatic nitriles is frequently weak or absent, but the $P + 1$ peak can usually be located by its behavior on increasing sample pressure or decreasing repeller voltage as already noted (pp. 10,11). The base peak (mass 41) of straight-chain nitriles higher than propionitrile (up to C_{10}) is usually formed by cleavage of the bond beta to the C≡N group with rearrangement of a hydrogen atom; the charge stays with the nitrogen-containing fragment.

A characteristic series of homologous peaks of even mass number (40, 54, 68, 82, and so forth) is produced by single cleavage at different bonds in the carbon chain, the charge remaining with the nitrogen-containing fragment. This series persists to $P - 1$.

Nitro Compounds,[9,40,41]

Aliphatic Nitro Compounds

The parent peak (odd number) of aliphatic nitro compounds is weak or absent (except for nitromethane). The main peaks are attributable to the hydrocarbon fragments. Presence of a nitro group is shown by an appreciable peak at mass 30 (NO^+) and at mass 46 (NO_2^+).

Aromatic Nitro Compounds

The parent peak (odd number) of aromatic nitro compounds is strong. Other prominent peaks appear at $P - 30$ (loss of NO with rearrangement), and $P - 46$ (loss of NO_2) and at mass 30 (NO^+).

Aliphatic Nitrites[42]

The parent peak (odd number) of aliphatic nitrites is weak or absent. The peak at mass 30 (NO^+) is always large and is often the base peak. There is a large peak at mass 60 (CH_2ONO^+) in all nitrites unbranched at the α-carbon atom; this represents cleavage of the bond beta to the ONO group. Absence of a large peak at mass 46 permits differentiation from nitro compounds. Hydrocarbon peaks are prominent and their distribution and intensities describe the configuration of the carbon chain.

Aliphatic Nitrates[9,41]

The parent peak (odd number) of aliphatic nitrates is weak or absent. A prominent (frequently the base) peak is formed by cleavage of the bond beta to the NO_2 group with loss of the heaviest alkyl group attached to the α-carbon.

The NO_2^+ peak at mass 46 is also prominent. As in the case of aliphatic nitrites, the hydrocarbon fragment ions are distinct.

Aliphatic Sulfur Compounds

The contribution of the S^{34} isotope to the $P + 2$ peak, and often to a fragment +2 peak, affords ready recognition of sulfur-containing compounds. A homologous series of sulfur-containing fragments is four mass units higher than the comparable hydrocarbon fragment series. The $P + 1$ peak is still useful for arriving at the empirical formula of the rest of the molecules after subtracting the sulfur mass. In Compound 6–5, for example, the molecular weight is 206, and the molecule contains 2 sulfur atoms. The empirical formula for the rest of the molecule is found under mass 142 ($206 - 64$). The contribution of the S^{33} isotope is subtracted from the $P + 1$ peak.

Aliphatic Mercaptans[9,43]

The parent peak of aliphatic mercaptans is distinct, as is the $P + 2$ peak. Cleavage of the bond beta to the sulfur atom gives the base peak of mass 47 (CH_2SH) for straight-chain primary mercaptans which also show a peak (of about one-half the intensity of the mass 47 peak) at mass 61, resulting from γ-cleavage. Primary mercaptans split out H_2S to give a large $P - 34$ peak.

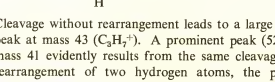
A large peak at mass 47 is also present as a rearrangement peak in many secondary and tertiary mercaptans. In general, secondary and tertiary mercaptans cleave beta to the sulfur atom with loss of the largest alkyl group. A peak at $P - 33$ (loss of SH rather than H_2S as in primary mercaptans) is usually present in secondary mercaptans.

Aliphatic Sulfides[9,43]

The parent peak of aliphatic sulfides is distinct as is the $P + 2$ peak. Fragmentation patterns are similar to those of aliphatic ethers, cleavage of the beta bond in the larger alkyl group being favored. Absence of peaks at $P - 33$ or $P - 34$ distinguishes sulfides from isomeric mercaptans.

Aliphatic Disulfides[9]

Only a few disulfide spectra have been reported. The parent peak (at least up to C_4 disulfides) is intense (it is the base peak in dimethyl disulfide). The base peak (mass 80) in methyl propyl disulfide results from cleavage between the S atom and the larger alkyl chain with rearrangement of one hydrogen atom, the charge remaining on the sulfur-containing fragment.



Cleavage without rearrangement leads to a large (67%) peak at mass 43 ($C_3H_7^+$). A prominent peak (52%) at mass 41 evidently results from the same cleavage with rearrangement of two hydrogen atoms, the positive change remaining on the nonsulfur fragment ($C_3H_5^+$). Other strong peaks result from cleavage between the sulfur atoms without rearrangement, and with rearrangement of one or two atoms of hydrogen to give CH_3S^+ (19%), CH_2S^+ (17%) and CHS^+ (40%).

Chlorine Bromine and Iodine Compounds[9,44–49]

Aliphatic Chlorine, Bromine, and Iodine Compounds

A compound which contains one chlorine atom will have a $P + 2$ peak approximately one-third the intensity of the parent peak because of the presence of molecular ions containing the Cl^{37} isotope. A compound which contains one bromine atom will have a $P + 2$ peak almost equal in intensity to the parent peak because of the presence of molecular ions containing the Br^{81} isotope. A compound which contains two chlorines, or two bromines, or one chlorine and one bromine, will show a distinct $P + 4$ peak because of the presence of molecular ions containing two atoms of the heavy isotope. In general, the number of chlorine and/or bromine atoms in a molecule can be ascertained by the number of alternate peaks beyond the parent peak. Thus, three Cl atoms in a molecule will give peaks at $P + 2$, $P + 4$, and $P + 6$; in polychloro compounds, the peak of highest mass may be so weak as to escape notice.

The relative abundances of the peaks (parent, $P + 2$ $P + 4$, and so forth) have been calculated by Beynon[44] for compounds containing chlorine and bromine (atoms other than chlorine and bromine were ignored.) A portion of these calculations is presented here, somewhat modified, as Table II. We can now tell what combination

Table II Intensities of Isotope Peaks (Relative to the Parent Peak) for Combinations of Bromine and Chlorine

HALOGEN PRESENT	% $P + 2$	% $P + 4$	% $P + 6$	% $P + 8$	% $P + 10$	% $P + 12$
Br	97.7	...	...	...	...	...
Br_2	195.0	95.5	...	...	...	...
Br_3	293.0	286.0	93.4	...	...	...
Cl	32.6	...	...	...	...	...
Cl_2	65.3	10.6	...	...	...	...
Cl_3	99.8	31.9	3.47	...	...	...
Cl_4	131.0	63.9	14.0	1.15	...	...
Cl_5	163.0	106.0	34.7	5.66	0.37	...
Cl_6	196.0	161.0	69.4	17.0	2.23	0.11
BrCl	130.0	31.9	...	...	...	...
Br_2Cl	228.0	159.0	31.2	...	...	...
Cl_2Br	163.0	74.4	10.4	...	...	...

of chlorine and bromine atoms is present. It should be noted that Table II presents the isotope contributions in terms of per cent of the parent peak.

Iodine has no heavy isotope; its presence can sometimes be deduced by a large interval between prominent peaks and by a small $P + 1$ peak in relation to the molecular weight.

The parent + 1 peak is still useful for arriving at an empirical formula by use of Appendix A, after subtracting the masses of the appropriate number of chlorine and bromine atoms. The odd-numbered isotope peaks are present, mainly because of C^{13} isotope contributions (see Compound 7–8).

Unfortunately, the application of isotope contributions, though generally useful for aromatic halogen compounds is limited by the weak parent peak of many aliphatic halogen compounds of more than six carbon atoms. Prominent peaks are usually found at $P - X$, $P - HX$, and $P - H_2X$. Each of these peaks is, of course, followed by peaks due to isotope contributions of the remaining chlorine or bromine atoms. The general appearance of spectra of long-chain aliphatic monohalogen compounds is similar to that of the corresponding hydrocarbons.

Aromatic Chlorine, Bromine, and Iodine Compounds

The parent peak of aromatic halogen compounds is readily apparent. The $P - X$ peak is large for all compounds in which X is attached directly to the ring. Cleavage of bonds beta to the ring predominates, especially when the halogen atom is the β-atom.

Fluorine Compounds[50,51]

The fluorine atom has no heavy isotope. Its presence can usually be deduced in highly fluorinated compounds from the small size of the parent + 1 peak in relation to the molecular weight, and by the unusual peaks in the fragmentation pattern. Sometimes the presence of fluorine is undetected until the mass of the rest of the molecule is subtracted from the molecular weight. See Compound 6–17. Perfluorinated saturated hydrocarbons all give a base peak at mass 69 (CF_3^+) and prominent peaks are usually present at 119, 169, 219, and so forth (increments of CF_2). The stable fragments $C_3F_5^+$ and $C_4F_7^+$ give large peaks at 131 and 181.

The parent peak is usually undetectable in highly fluorinated aliphatic compounds, but the $P - F$ peak is prominent in small fluorocarbon molecules. The parent peak of aromatic fluorine compounds is usually strong.

Heteroaromatic Compounds[9,52]

The heteroaromatic ring (furan, thiophene, pyrrole, pyridine, indole, and so forth) has the same effects on an alkyl chain as does the benzene ring: It promotes cleavage of the bond beta to the ring (Rule 7) and leads to a prominent parent peak (Rule 4). The parent peak is usually strong.

References

1. Beynon, J. H., *Mass Spectrometry and Its Application to Organic Chemistry*, Elsevier, Amsterdam, 1960.
2. Stewart, D. W., "Mass Spectrometry," in Weissberger, ed., *Technique of Organic Chemistry*, Vol. 1, Part IV, 3rd ed., Interscience, New York, 1960, pp. 3449–3539.
3. Dibeler, V. H., "Analytical Mass Spectrometry," in Mitchell, ed., *Organic Analysis*, Vol. III, Interscience, New York, 1956, pp. 387–441.
4. Duckworth, H. E., *Mass Spectroscopy*, University Press, Cambridge, England, 1958.
5. Waldron, J. D., ed., *Advances in Mass Spectrometry*, Pergamon Press, London, 1959.
6. Wien, W., *Ann. Physik*, **65,** 440 (1898).
7. Thomson, J. J., *Phil. Mag.*, **10,** 584 (1905).
8. Gohlke, R. S., *Anal. Chem.*, **31,** 535 (1959).
9. "Catalog of Mass Spectra Data," American Petroleum Institute Res. Project No. 44, Carnegie Institute of Technology, Pittsburgh, Penn.
10. McLafferty, F. W., *Anal. Chem.*, **31,** 82 (1959).
11. Coulson, D. M., and L. A. Cavanaugh, *Anal. Chem.*, **32,** 1245 (1960).
12. Friedel, R. A., J. L. Shultz, and A. G. Sharkey, Jr., *Anal. Chem.*, **28,** 926 (1956).
13. McLafferty, F. W., *Anal. Chem.*, **29,** 1782 (1957).
14. Eden, M., B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23,** 1735 (1951).
15. Sharkey, A. G., R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29,** 770 (1957).
16. Langer, S. H., S. Connell, and I. Wender, *J. Org. Chem.*, **23,** 50 (1958).
17. Siegel, H., and D. O. Schissler, *Anal. Chem.*, **28,** 1646 (1956).
18. Biemann, K., F. Gapp, and J. Seibl, *J. Am. Chem. Soc.*, **81,** 2274 (1959).
19. Biemann, K., J. Seibl, and F. Gapp, *J. Am. Chem. Soc.*, **83,** 3795 (1961).
20. Bloom, E. G., F. L. Mohler, J. H. Tengel, and C. E. Wise, *J. Res. Nat. Bur. Standards*, **41,** 129 (1948).
21. Brown, R. A., *Anal. Chem.*, **23,** 430 (1951).
22. Friedel, R. A., A. F. Logar, and J. L. Schultz, *Appl. Spectroscopy*, **6,** No. 5, 24 (1952).
23. Kinney, I. W., Jr., and G. L. Cook, *Anal. Chem.*, **24,** 1391 (1954).
24. O'Neal, M. J., Jr., and T. P. Wier, Jr., *Anal. Chem.*, **23,** 830 (1951).
25. Washburn, H. W., *Physical Methods in Chemical Analysis* W. G. Berl, ed., Academic Press, New York, 1950, p. 592.
26. Rylander, P. N., S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79,** 842 (1957).
27. Meyerson, S., and P. N. Rylander, *J. Chem. Phys.*, **27,** 901 (1957).
28. Yarborough, V. A., *Anal. Chem.*, **25,** 1914 (1953).
29. Brown, R. A., W. S. Young, and N. Nicolaides, *Anal. Chem.*, **26,** 1653 (1954).
30. Friedel, R. A., and A. G. Sharkey, *Anal., Chem.*, **28,** 940 (1956).
31. Sharkey, A. G., J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **28,** 934 (1956).
32. Gilpin, J. A., and F. W. McLafferty, *Anal. Chem.*, **29,** 990 (1957).
33. Happ, G. P., and D. W. Stewart, *J. Am. Chem. Soc.*, 74, 4404 (1952).
34. Gohlke, R. S., and F. W. McLafferty, 4th Annual Meeting, ASTM Committee E-14, San Francisco, Calif. (1955).
35. Sharkey, A. G., Jr., J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **31,** 87 (1959).
36. Asselineau, J., R. Ryhage and E. Stenhagen, *Acta. Chem. Scand.* **11,** 196 (1957).
37. Collins, J., *Bull. soc. roy. sci. Liège*, **21,** 446 (1952).
38. Gilpin, J. A., *Anal. Chem.*, **31,** 935 (1959).
39. McLafferty, F. W., 4th Annual Meeting, ASTM Committee E-14 Cincinnati, Ohio (1956). McLafferty, F. W., *Anal. Chem.*, **34,** 26 (1962).
40. Collins, J., *Bull. soc. roy. sci. Liège*, **23,** 194 (1954).
41. Boschan, R., and S. R. Smith, U.S. Govt. Dept. of Comm. Office of Tech. Service, PB 151120, July 1957.
42. D'Or, L., and J. Collins, *Bull. soc. roy. soc. Liège*, **22,** 285 (1953).
43. Levy, E. J., and W. A. Stahl, 5th Annual Meeting, ASTM Committee E-14, New York (1957).
44. Beynon, *op. cit.*, p. 298.
45. McLafferty, F. W., 3rd Annual Meeting, ASTM Committee E-14, San Francisco, Calif. (1955). McLafferty, F. W., *Anal. Chem.*, **34,** 2, 16 (1962).
46. Irsa, A. P., *J. Chem. Phys.*, **26,** 18 (1957).
47. Momigny, J., *Bull. soc. chim. Belges*, **64,** 144 (1955).
48. D'Or, L., H. Neyns, and J. Momigny, *Ann. soc. sci. Bruxelles*, **71,** (Ser. 1) 53 (1957).
49. Tayler, R. C., R. A. Brown, W. S. Young, and C. E. Headington, *Anal. Chem.*, **20,** 396 (1948).
50. Mohler, F. L., E. G. Bloom, J. N. Lengel, and C. E. Wise, *J. Am. Chem. Soc.*, **71,** 337 (1949).
51. Mohler, F. L., V. H. Dibeler, and R. M. Reese, *J. Research*, NBS, **49,** 343 (1952).
52. Beynon, J. H., and A. E. Williams, *Appl. Spectroscopy*, **13,** 101 (1959).
53. McLafferty, F. W., *Mass Spectrometry*, Chapt. 2, Vol. II, "Determination of Organic Structure by Physical Methods," by

F. C. Nachod and W. D. Phillips (ed.), Academic Press, New York, 1962. The discussion of mechanisms of rearrangements is especially thorough.

54. Biemann, K., *Mass Spectrometry, Applications to Organic Chemistry*, McGraw-Hill, New York, 1962. This is the first book on mass spectrometry addressed entirely to the organic chemist. The emphasis is on structure determinations of complex molecules.

References 53–56 are recent general references added in proof.

55. *Bibliography on Mass Spectrometry*, 1938–1957 inclusive, Associated Electrical Industries, Ltd., Instrumentation Division, Pergamon Press, London, 1961.

56. Djerassi, C., H. W. Brewer, H. Budzekiewicz, O. O. Orazi, and R. A. Corral, *J. Am. Chem. Soc.*, **84,** 3480 (1962). The utility of mass spectrometry together with NMR to determine structures of complex alkaloids was demonstrated. Assignment of mass fragments was confirmed by deuteration.

APPENDIX A Masses and Isotopic Abundance Ratios for Various Combinations of Carbon, Hydrogen, Nitrogen and Oxygen*

	P + 1	P + 2
12		
C	1.08	
13		
CH	1.10	
14		
N	0.38	
CH_2	1.11	
15		
NH	0.40	
CH_3	1.13	
16		
O	0.04	0.20
NH_2	0.41	
CH_4	1.15	
17		
OH	0.06	0.20
NH_3	0.43	
CH_5	1.16	
18		
H_2O	0.07	0.20
NH_4	0.45	
19		
H_3O	0.09	0.20
24		
C_2	2.16	0.01
25		
C_2H	2.18	0.01
26		
CN	1.46	
C_2H_2	2.19	0.01
27		
CHN	1.48	
C_2H_3	2.21	0.01
28		
N_2	0.76	
CO	1.12	0.02
CH_2N		
C_2H_4		
29		
N_2H		
CHO		
CH_3N		
C_2H_5		
30		
NO		
N_2H_2		
CH_2O		
CH_4N		
C_2H_6		
31		
NOH		
N_2H_3		
CH_3O		
CH_5N		
32		
O_2		
NOH_2		
N_2H_4		
CH_4O		
33		
NOH_3		
N_2H_5		
CH_5O		
34		
N_2H_6		
36		
C_3		
37		
C_3H		
38		
C_2N		
C_3H_2		
39		
C_2HN		
C_3H_3		

	P + 1	P + 2
1.49		
2.23	0.01	
0.78		
1.14	0.20	
1.51		
2.24	0.01	
0.42	0.20	
0.79		
1.15	0.20	
1.53	0.01	
2.26	0.01	
0.44	0.20	
0.81		
1.17	0.20	
1.54		
0.08	0.40	
0.45	0.20	
0.83		
1.18	0.20	
0.47	0.20	
0.84		
1.12		
0.86		
3.24	0.04	
3.26	0.04	
2.54	0.02	
3.27	0.04	
2.56	0.02	
3.29	0.04	

	P + 1	P + 2
40		
CN_2	1.84	0.01
C_3O	2.20	0.21
C_2H_2N	2.58	0.02
C_3H_4	3.31	0.04
41		
CHN_2	1.86	
C_2HO	2.22	0.21
C_2H_3N	2.59	0.02
C_3H_5	3.32	0.04
42		
CNO	1.50	0.21
CH_2N_2	1.88	0.01
C_2H_2O	2.23	0.21
C_2H_4N	2.61	0 02
C_3H_6	3.34	0.04
43		
CHNO	1.52	0.21
CH_3N_2	1.89	0.01
C_2H_3O	2.25	0.21
C_2H_5N	2.62	0.02
C_3H_7	3.35	0.04
44		
N_2O	0.80	0.20
CO_2	1.16	0.40
CH_2NO	1.53	0.21
CH_4N_2	1.91	0.01
C_2H_4O	2.26	0.21
C_2H_6N	2.64	0.02
C_3H_8	3.37	0.04
45		
HN_2O	0.82	0.20
CHO_2	1.18	0.40
CH_3NO	1.55	0.21
CH_5N_2	1.92	0.01
C_2H_5O	2.28	0.21
C_2H_7N	2.66	0.02
46		
NO_2	0.46	0.40
N_2H_2O	0.83	0.20
CH_2O_2	1.19	0.40
CH_4NO	1.57	0.21
CH_6N_2	1.94	0.01

	P + 1	P + 2
C_2H_6O	2.30	0.22
C_2H_8N	2.66	0.02
47		
CH_3O_2	1.21	0.40
CH_5NO	1.58	0.21
CH_7N_2	1.96	0.01
C_2H_7O	2.31	0.22
48		
CH_4O_2	1.22	0.40
C_4	4.32	0.07
49		
CH_5O_2	1.24	0.40
C_4H	4.34	0.07
50		
C_4H_2	4.34	0.07
51		
C_4H_3	4.37	0.07
52		
C_2N_2	2.92	0.03
C_3H_2N	3.66	0.05
C_4H_4	4.39	0.07
53		
C_2HN_2	2.94	0.03
C_3HO	3.30	0.24
C_3H_3N	3.67	0.05
C_4H_5	4.40	0.07
54		
C_2NO	2.58	0.22
$C_2H_2N_2$	2.96	0.03
C_3H_2O	3.31	0.24
C_3H_4N	3.69	0.05
C_4H_6	4.42	0.07
55		
C_2HNO	2.60	0.22
$C_2H_3N_2$	2.97	0.03
C_3H_3O	3.33	0.24
C_3H_5N	3.70	0.05
C_4H_7	4.43	0.08

* Adapted with permission from J. H. Beynon, *Mass Spectrometry and Its Application to Organic Chemistry*, Elsevier, Amsterdam, 1960.

	P + 1	P + 2
56		
CH_2N_3	2.26	0.02
C_2O_2	2.24	0.41
C_2H_2NO	2.61	0.22
$C_2H_4N_2$	2.99	0.03
C_3H_4O	3.35	0.24
C_3H_6N	3.72	0.05
C_4H_8	4.45	0.08
57		
CHN_3O	1.90	0.21
CH_3N_3	2.27	0.02
C_2HO_2	2.26	0.41
C_2H_3NO	2.63	0.22
$C_2H_5N_2$	3.00	0.03
C_3H_5O	3.36	0.24
C_3H_7N	3.74	0.05
C_4H_9	4.47	0.08
58		
CNO_2	1.54	0.41
CH_2N_2O	1.92	0.21
CH_4N_3	2.29	0.02
$C_2H_2O_2$	2.27	0.42
C_2H_4NO	2.65	0.22
$C_2H_6N_2$	3.02	0.03
C_3H_6O	3.38	0.24
C_3H_8N	3.75	0.05
C_4H_{10}	4.48	0.08
59		
$CHNO_2$	1.56	0.41
CH_3N_2O	1.93	0.21
CH_5N_3	2.31	0.02
$C_2H_3O_2$	2.29	0.42
C_2H_5NO	2.66	0.22
$C_2H_7N_2$	3.04	0.03
C_3H_7O	3.39	0.24
C_3H_9N	3.77	0.05
60		
CH_2NO_2	1.57	0.41
CH_4N_2O	1.95	0.21
CH_6N_3	2.32	0.02
$C_2H_4O_2$	2.30	0.04
C_2H_6NO	2.68	0.22
$C_2H_8N_2$	3.05	0.03
C_3H_8O	3.41	0.24
61		
CHO_3	1.21	0.60
CH_3NO_2	1.59	0.41
CH_5N_2O	1.96	0.21
CH_7N_3	2.34	0.02
$C_2H_5O_2$	2.32	0.42
C_2H_7NO	2.69	0.22
C_3H_9O	3.43	0.24
C_5H	5.42	0.12
62		
CH_2O_3	1.23	0.60
CH_4NO_2	1.60	0.41
CH_6N_2O	1.98	0.21
CH_8N_3	2.35	0.02
$C_2H_6O_2$	2.34	0.42
C_5H_2	5.44	0.12
63		
CH_3O_3	1.25	0.60
CH_5NO_2	1.62	0.41
C_4HN	4.72	0.09
C_5H_3	5.45	0.12
64		
CH_4O_3	1.26	0.60
C_4H_2N	4.74	0.09
C_5H_4	5.47	0.12
65		
C_3HN_2	4.02	0.06
C_4HO	4.38	0.27
C_4H_3N	4.75	0.09
C_5H_5	5.48	0.12
66		
$C_3H_2N_2$	4.04	0.06
C_4H_2O	4.39	0.27
C_4H_4N	4.77	0.09
C_5H_6	5.50	0.12
67		
C_2HN_3	3.32	0.04
C_3HNO	3.68	0.25
$C_3H_3N_2$	4.05	0.06
C_4H_3O	4.41	0.27
C_4H_5N	4.78	0.09
C_5H_7	5.52	0.12
68		
$C_2H_2N_3$	3.34	0.04
C_3O_2	3.32	0.44
C_3H_2NO	3.69	0.25
$C_3H_4N_2$	4.07	0.06
C_4H_4O	4.43	0.28
C_4H_6N	4.80	0.09
C_5H_8	5.53	0.12
69		
CHN_4	2.62	0.03
C_2HN_2O	2.98	0.23
$C_2H_3N_3$	3.35	0.04
C_3HO_2	3.34	0.44
C_3H_3NO	3.71	0.25
$C_3H_5N_2$	4.09	0.06
C_4H_5O	4.44	0.28
C_4H_7N	4.82	0.09
C_5H_9	5.55	0.12
70		
CH_2N_4	2.64	0.03
C_2NO_2	2.62	0.42
$C_2H_2N_2O$	3.00	0.23
$C_2H_4N_3$	3.37	0.04
$C_3H_2O_2$	3.35	0.44
C_3H_4NO	3.73	0.25
$C_3H_6N_2$	4.10	0.07
C_4H_6O	4.46	0.28
C_4H_8N	4.83	0.09
C_5H_{10}	5.56	0.13
71		
CHN_3O	2.28	0.22
CH_3N_4	2.65	0.03
C_2HNO_2	2.64	0.42
$C_2H_5N_2O$	3.01	0.23
$C_3H_5N_2$	3.39	0.04
$C_3H_7O_2$	3.37	0.44
C_3H_7NO	3.74	0.25
$C_3H_7N_2$	4.12	0.07
C_4H_7O	4.47	0.28
C_4H_9N	4.85	0.09
C_5H_{11}	5.58	0.13
72		
CH_2N_2O	2.30	0.22
CH_4N_4	2.67	0.03
$C_2H_2NO_2$	2.65	0.42
$C_2H_4N_2O$	3.03	0.23
$C_2H_6N_3$	3.40	0.44
$C_3H_4O_2$	3.38	0.44
C_3H_6NO	3.76	0.25
$C_3H_8N_2$	4.13	0.07
C_4H_8O	4.49	0.28
$C_4H_{10}N$	4.86	0.09
C_5H_{12}	5.60	0.13
73		
CHN_2O_2	1.94	0.41
CH_3N_3O	2.31	0.22
CH_5N_4	2.69	0.03
C_2HO_3	2.30	0.62
$C_2H_3NO_2$	2.67	0.42
$C_2H_5N_2O$	3.04	0.23
$C_2H_7N_3$	3.42	0.04
$C_3H_5O_2$	3.40	0.44
C_3H_7NO	3.77	0.25
$C_3H_9N_2$	4.15	0.07
C_4H_9O	4.51	0.28
$C_4H_{11}N$	4.88	0.10
C_6H	6.50	0.18
74		
$CH_2N_2O_2$	1.95	0.41
CH_4N_3O	2.33	0.22
CH_6N_4	2.70	0.03
$C_2H_2O_3$	2.31	0.62
$C_2H_4NO_2$	2.69	0.42
$C_2H_6N_2O$	3.06	0.23
$C_2H_8N_3$	3.43	0.05
$C_3H_6O_2$	3.42	0.44
C_3H_8NO	3.79	0.25
$C_3H_{10}N_2$	4.17	0.07
$C_4H_{10}O$	4.52	0.28
C_6H_2	6.52	0.18
75		
$CHNO_3$	1.60	0.61
$CH_3N_2O_2$	1.97	0.41
CH_5N_3O	2.34	0.22
CH_7N_4	2.72	0.03
$C_2H_3O_3$	2.33	0.62
$C_2H_5NO_2$	2.70	0.43
$C_2H_7N_2O$	3.08	0.23
$C_2H_9N_3$	3.45	0.05
$C_3H_7O_2$	3.43	0.44
C_3H_9NO	3.81	0.25
C_5HN	5.80	0.14
C_6H_3	6.53	0.18
76		
CH_4NO_3	1.61	0.61
$CH_4N_2O_2$	1.99	0.41
CH_6N_3O	2.36	0.22
CH_8N_4	2.73	0.03
$C_2H_4O_3$	2.34	0.62
$C_2H_6NO_2$	2.72	0.43
$C_2H_8N_3O$	3.09	0.24
$C_3H_8O_2$	3.45	0.44
C_5H_2N	5.82	0.14
C_6H_4	6.55	0.18
77		
CHO_4	1.25	0.80
CH_3NO_3	1.63	0.61
$CH_5N_2O_2$	2.00	0.41
CH_7N_3O	2.38	0.22
$C_2H_5O_3$	2.39	0.62
$C_2H_7NO_2$	2.73	0.43
C_4HN_2	5.10	0.11
C_5HO	5.45	0.32
C_5H_3N	5.83	0.14
C_6H_5	6.56	0.18
78		
CH_2O_4	1.27	0.80
CH_4NO_3	1 64	0.61
$CH_6N_2O_2$	2.02	0.41
$C_2H_6O_3$	2.38	0.62
$C_4H_2N_2$	5.12	0.11
C_5H_2O	5.47	0.32
C_5H_4N	5.49	0.14
C_6H_6	6.58	0.18
79		
CH_3O_4	1.29	0.80
CH_5NO_3	1.66	0.61
C_5HN_2	4.40	0.08
C_4HNO	4.76	0.29
$C_4H_3N_2$	5.13	0.11
C_5H_3O	5.49	0.32
C_5H_5N	5.87	0.14
C_6H_7	6.60	0.18
80		
CH_4O_4	1.30	0.80
$C_3H_2N_3$	4.42	0.08
C_4H_2NO	4.78	0.29
$C_4H_4N_2$	5.15	0.11
C_5H_4O	5.51	0.32
C_5H_6N	5.88	0.14
C_6H_8	6.61	0 18
81		
C_2HN_4	3.70	0.05
C_3HN_2O	4.06	0 26

	P + 1	P + 2
$C_3H_9N_3$	4.43	0.08
C_4HO_2	4.42	0.48
C_4H_3NO	4.79	0.29
$C_4H_5N_2$	5.17	0.11
C_5H_5O	5.52	0.32
C_5H_7N	5.90	0.14
C_6H_9	6.63	0.18
82		
$C_2H_2N_4$	3.72	0.05
$C_3H_2N_2O$	4.08	0.36
$C_4H_4N_2$	4.45	0.08
$C_4H_2O_2$	4.43	0.48
C_4H_4NO	4.81	0.29
$C_4H_6N_2$	4.18	0.11
C_5H_6O	5.54	0.32
C_5H_8N	5.91	0.14
C_6H_{10}	6.64	0.19
83		
C_2HN_3O	3.36	0.24
$C_2H_3N_4$	3.74	0.06
C_3HNO_2	3.72	0.45
$C_3H_3N_2O$	4.09	0.27
$C_3H_5N_3$	4.47	0.08
$C_4H_3O_2$	4.45	0.48
C_4H_5NO	4.82	0.29
$C_4H_7N_2$	5.20	0.11
C_5H_7O	5.55	0.33
C_5H_9N	5.93	0.15
C_6H_{11}	6.66	0.19
84		
$C_2H_2N_3O$	3.38	0.24
$C_2H_4N_4$	3.75	0.06
$C_3H_2NO_2$	3.73	0.45
$C_3H_4N_2O$	4.11	0.27
$C_3H_6N_3$	4.48	0.81
$C_4H_4O_2$	4.47	0.48
C_4H_6NO	4.84	0.29
$C_4H_8N_2$	5.21	0.11
C_5H_8O	5.57	0.33
$C_5H_{10}N$	5.95	0.15
C_6H_{12}	6.68	0.19
85		
CHN_4O	2.66	0.23
$C_2HN_2O_2$	3.02	0.43
$C_2H_3N_4O$	3.39	0.24
$C_2H_5N_4$	3.77	0.06
C_3HO_3	3.38	0.64
$C_3H_3NO_2$	3.75	0.45
$C_3H_5N_2O$	4.12	0.27
$C_3H_7N_3$	4.50	0.08
$C_4H_5O_2$	4.48	0.48
C_4H_7NO	4.86	0.29
$C_4H_9N_2$	5.23	0.11
C_5H_9O	5.59	0.33
$C_5H_{11}N$	5.96	0.15
C_6H_{13}	6.69	0.19
C_7H	7.58	0.25
86		
CH_2N_4O	2.68	0.23
$C_2H_2N_2O_2$	3.03	0.43
$C_2H_4N_4O$	3.41	0.24
$C_2H_6N_4$	3.78	0.06
$C_3H_2O_3$	3.39	0.64
$C_3H_4NO_2$	3.77	0.45
$C_3H_6N_2O$	4.14	0.27
$C_3H_8N_3$	4.51	0.08
$C_4H_6O_2$	4.50	0.48
C_4H_8NO	4.87	0.30
$C_4H_{10}N_2$	5.25	0.11
$C_5H_{10}O$	5.60	0.33
$C_5H_{12}N$	5.98	0.15
C_6H_{14}	6.71	0.19
C_7H_2	7.60	0.25
87		
CHN_2O_2	2.32	0.42
CH_3N_4O	2.69	0.23
C_2HNO_3	2.68	0.62
$C_2H_3N_2O_2$	3.05	0.43
$C_2H_5N_3O$	3.43	0.25
$C_2H_7N_4$	3.80	0.06
$C_3H_3O_3$	3.41	0.64
$C_3H_5NO_2$	3.78	0.45
$C_3H_7N_2O$	4.16	0.27
$C_3H_9N_3$	4.53	0.08
$C_4H_7O_2$	4.51	0.48
C_4H_9NO	4.89	0.30
$C_4H_{11}N_2$	5.26	0.11
$C_5H_{11}O$	5.62	0.33
$C_5H_{13}N$	5.99	0.15
C_6HN	6.88	0.20
C_7H_3	7.61	0.25
88		
$CH_2N_4O_2$	2.34	0.42
CH_4N_4O	2.71	0.23
$C_2H_2NO_3$	2.69	0.63
$C_2H_4N_2O_2$	3.07	0.43
$C_2H_6N_4O$	3.44	0.25
$C_3H_8N_4$	3.82	0.06
$C_3H_4O_3$	3.42	0.64
$C_3H_6NO_2$	3.80	0.45
$C_3H_8N_2O$	4.17	0.27
$C_3H_{10}N_3$	4.55	0.08
$C_4H_8O_2$	4.53	0.48
$C_4H_{10}NO$	4.90	0.30
$C_4H_{12}N_2$	5.28	0.11
$C_5H_{12}O$	5.63	0.33
$C_6H_{14}N$	6.90	0.20
C_7H_4	7.63	0.25
89		
CHN_2O_3	1.98	0.61
$CH_3N_2O_2$	2.35	0.42
CH_5N_4O	2.73	0.23
C_2HO_4	2.33	0.82
$C_2H_3NO_3$	2.71	0.63
$C_2H_5N_2O_2$	3.08	0.44
$C_2H_7N_4O$	3.46	0.25
$C_2H_9N_4$	3.83	0.06
$C_3H_5O_3$	3.44	0.64
$C_3H_7NO_2$	3.81	0.46
$C_3H_9N_2O$	4.19	0.27
$C_3H_{11}N_3$	4.56	0.84
$C_4H_9O_2$	4.55	0.48
$C_4H_{11}NO$	4.92	0.30
$C_5H_{13}N_2$	6.18	0.16
C_6HO	6.54	0.38
C_6H_9N	6.91	0.20
C_7H_5	7.64	0.25
90		
$CH_2N_2O_3$	1.99	0.61
$CH_4N_4O_2$	2.37	0.42
CH_6N_4O	2.74	0.23
$C_2H_2O_4$	2.35	0.82
$C_2H_4NO_3$	2.72	0.63
$C_2H_6N_3O_2$	3.10	0.44
$C_2H_8N_4O$	3.47	0.25
$C_2H_{10}N_4$	3.85	0.06
$C_3H_6O_3$	3.46	0.64
$C_3H_8NO_2$	3.83	0.46
$C_3H_{10}N_2O$	4.20	0.27
$C_4H_{10}O_2$	4.56	0.48
$C_5H_{12}N_2$	6.20	0.16
$C_6H_{14}O$	6.56	0.38
$C_6H_{16}N$	6.93	0.20
C_7H_8	7.66	0.25
91		
$CHNO_4$	1.63	0.81
$CH_3N_2O_3$	2.01	0.61
$CH_5N_4O_2$	2.38	0.42
CH_7N_4O	2.76	0.23
$C_2H_3O_4$	2.37	0.82
$C_2H_5NO_3$	2.74	0.63
$C_2H_7N_2O_2$	3.11	0.44
$C_2H_9N_4O$	3.49	0.25
$C_3H_7O_3$	3.47	0.64
$C_3H_9NO_2$	3.85	0.46
C_4HN_3	5.48	0.12
C_5HNO	5.84	0.34
$C_5H_3N_2$	6.21	0.16
C_6H_9O	6.57	0.38
C_6H_5N	6.95	0.21
C_7H_7	7.68	0.25
92		
CH_2NO_4	1.65	0.81
$CH_4N_2O_3$	2.03	0.61
$CH_6N_4O_2$	2.40	0.42
CH_8N_4O	2.77	0.23
$C_2H_4O_4$	2.38	0.82
$C_2H_6NO_3$	2.76	0.63
$C_2H_8N_2O_2$	3.13	0.44
$C_2H_{10}N_4O$	3.49	0.64
$C_3H_6O_3$	5.50	0.13
$C_4H_2N_3$	5.86	0.34
C_5H_4NO	6.23	0.16
C_6H_8O	6.59	0.38
C_6H_8N	6.96	0.21
C_7H_8	7.69	0.26
N_2O_4	9.19	0.80
93		
CH_3NO_4	1.67	0.81
$CH_5N_2O_3$	2.04	0.61
$CH_7N_3O_2$	2.42	0.42
CH_9N_4O	2.40	0.82
$C_2H_3NO_4$	2.77	0.63
$C_2H_5N_3O_3$	4.78	0.09
$C_2H_7N_4O$	5.14	0.31
$C_2H_9N_4$	5.52	0.13
C_3HO_3	5.50	0.52
C_3H_3NO	5.87	0.34
$C_3H_5N_2$	6.25	0.16
C_4H_4O	6.60	0.38
C_4H_6N	6.98	0.21
C_5H_9	7.71	0.26
94		
CH_4NO_4	1.68	0.81
$CH_6N_2O_3$	2.06	0.62
$C_2H_6O_4$	2.41	0.82
$C_3H_2N_4$	4.80	0.09
$C_4H_2N_2O$	5.16	0.31
$C_4H_4N_3$	5.53	0.13
$C_5H_5O_2$	5.51	0.52
C_5H_7NO	5.89	0.34
C_6H_9N	6.26	0.17
$C_5H_6O_2$	6.62	0.38
C_6H_8N	6.99	0.21
C_7H_{10}	7.72	0.26
95		
CH_3NO_4	1.70	0.81
$C_3H_3N_3O$	4.44	0.28
$C_3H_5N_4$	4.82	0.10
C_4HNO_2	4.80	0.49
$C_4H_3N_2O$	5.17	0.31
$C_4H_5N_3$	5.55	0.13
$C_5H_3O_2$	5.53	0.52
C_5H_5NO	5.90	0.34
$C_5H_7N_2$	6.28	0.17
C_6H_7O	6.64	0.39
C_6H_9N	7.01	0.21
C_7H_{11}	7.74	0.26
96		
$C_3H_2N_3O$	4.46	0.28
$C_3H_4N_4$	4.83	0.10
$C_4H_2NO_2$	4.81	0.49
$C_4H_4N_3O$	5.19	0.31
$C_4H_6N_3$	5.56	0.13
$C_5H_4O_2$	5.55	0.53
C_5H_6NO	5.92	0.35
$C_5H_8N_2$	6.29	0.17
C_6H_8O	6.65	0.39
$C_6H_{10}N$	7.03	0.21
C_7H_{12}	7.76	0.26
97		
C_2HN_4O	3.74	0.26
$C_3HN_2O_2$	4.10	0.47
$C_3H_3N_3O$	4.47	0.28
$C_3H_5N_4$	4.85	0.10
C_4HO_3	4.46	0.68
$C_4H_3NO_2$	4.83	0.49
$C_4H_5N_2O$	5.20	0.31
$C_4H_7N_3$	5.58	0.13
$C_5H_5O_2$	5.56	0.53

	P + 1	P + 2
C_5H_7NO	5.94	0.35
$C_5H_9N_2$	6.31	0.17
C_6H_9O	6.67	0.39
$C_6H_{11}N$	7.04	0.21
C_7H_{13}	7.77	0.26
C_8H	8.66	0.33
98		
$C_2H_2N_4O$	3.76	0.26
$C_3H_2N_3O_2$	4.12	0.47
$C_3H_4N_3O$	4.49	0.28
$C_3H_2N_4$	4.86	0.10
$C_4H_2O_3$	4.47	0.68
$C_4H_4NO_2$	4.85	0.49
$C_4H_6N_2O$	5.22	0.31
$C_4H_8N_3$	5.60	0.13
$C_5H_6O_2$	5.58	0.53
C_5H_8NO	5.95	0.35
$C_5H_{10}N_2$	6.33	0.17
$C_6H_{10}O$	6.68	0.39
$C_6H_{12}N$	7.06	0.21
C_7H_{14}	7.79	0.26
C_8H_2	8.68	0.33
99		
$C_2HN_3O_2$	3.40	0.44
$C_2H_3N_4O$	3.77	0.26
C_3HNO_3	3.76	0.65
$C_3H_3N_2O_2$	4.13	0.47
$C_3H_5N_3O$	4.51	0.28
$C_3H_7N_4$	4.88	0.10
$C_4H_3O_3$	4.49	0.68
$C_4H_5NO_2$	4.86	0.50
$C_4H_7N_2O$	5.24	0.31
$C_4H_9N_3$	5.61	0.13
$C_5H_7O_2$	5.59	0.53
C_5H_9NO	5.97	0.35
$C_5H_{11}N_2$	6.34	0.17
$C_6H_{11}O$	6.70	0.39
$C_6H_{13}N$	7.07	0.21
C_7HN	7.96	0.28
C_7H_{15}	7.80	0.26
C_8H_3	8.69	0.33
100		
$C_2H_2N_3O_2$	3.42	0.45
$C_2H_4N_4O$	3.79	0.26
$C_3H_2NO_3$	3.77	0.65
$C_3H_4N_2O_2$	4.15	0.47
$C_3H_6N_3O$	4.52	0.28
$C_3H_8N_4$	4.90	0.10
$C_4H_4O_3$	4.50	0.68
$C_4H_6NO_2$	4.88	0.50
$C_4H_8N_2O$	5.25	0.31
$C_4H_{10}N_3$	5.63	0.13
$C_5H_8O_2$	5.61	0.53
$C_5H_{10}NO$	5.98	0.35
$C_5H_{12}N_2$	6.36	0.17
$C_6H_{12}O$	6.72	0.39
$C_6H_{14}N$	7.09	0.22
C_7H_2N	7.98	0.28
C_7H_{16}	7.82	0.26
C_8H_4	8.71	0.33
101		
CHN_4O_2	2.70	0.43
$C_2HN_2O_3$	3.06	0.64
$C_2H_3N_3O_2$	3.43	0.45
$C_2H_5N_4O$	3.81	0.26
C_3HO_4	3.41	0.84
$C_3H_3NO_3$	3.79	0.65
$C_3H_5N_2O_2$	4.16	0.47
$C_3H_7N_3O$	4.54	0.28
$C_3H_9N_4$	4.91	0.10
$C_4H_5O_3$	4.52	0.68
$C_4H_7NO_2$	4.89	0.50
$C_4H_9N_2O$	5.27	0.31
$C_4H_{11}N_3$	5.64	0.13
$C_5H_9O_2$	5.63	0.53
$C_5H_{11}NO$	6.00	0.35
$C_5H_{13}N_2$	6.37	0.17
C_6HN_2	7.26	0.23
$C_6H_{13}O$	6.73	0.39
$C_6H_{15}N$	7.11	0.22
C_7HO	7.62	0.45
C_7H_9N	7.99	0.28
C_8H_5	8.73	0.33
102		
$CH_2N_4O_2$	2.72	0.43
$C_2H_4N_2O_3$	3.07	0.64
$C_2H_6N_3O_2$	3.45	0.45
$C_2H_8N_4O$	3.82	0.26
$C_3H_2O_4$	3.43	0.84
$C_3H_4NO_3$	3.81	0.66
$C_3H_6N_2O_2$	4.18	0.47
$C_3H_8N_3O$	4.55	0.28
$C_3H_{10}N_4$	4.93	0.10
$C_4H_6O_3$	4.54	0.68
$C_4H_8NO_2$	4.91	0.50
$C_4H_{10}N_2O$	5.28	0.32
$C_4H_{12}N_3$	5.66	0.13
$C_5H_{10}O_2$	5.64	0.53
$C_5H_{12}NO$	6.02	0.35
$C_5H_{14}N_2$	6.39	0.17
$C_6H_2N_2$	7.28	0.23
$C_6H_{14}O$	6.75	0.39
C_7H_2O	7.64	0.45
$C_7H_{11}N$	8.01	0.28
C_8H_6	8.74	0.34
103		
CHN_3O_2	2.36	0.62
$CH_3N_4O_2$	2.73	0.43
C_2HNO_4	2.72	0.83
$C_2H_3N_2O_3$	3.09	0.64
$C_2H_5N_3O_2$	3.46	0.45
$C_2H_7N_4O$	3.84	0.26
$C_3H_5O_4$	3.45	0.84
$C_3H_5NO_3$	3.82	0.66
$C_3H_7N_2O_2$	4.20	0.47
$C_3H_9N_3O$	4.57	0.29
$C_3H_{11}N_4$	4.94	0.10
$C_4H_7O_3$	4.55	0.68
$C_4H_9NO_2$	4.93	0.50
$C_4H_{11}N_2O$	5.30	0.32
$C_4H_{13}N_3$	5.68	0.14
C_5HN_3	6.56	0.18
$C_5H_{11}O_2$	5.66	0.53
$C_5H_{13}NO$	6.03	0.35
C_6HNO	6.92	0.40
$C_6H_9N_2$	7.30	0.23
C_7H_9O	7.65	0.45
$C_7H_{11}N$	8.03	0.28
C_8H_7	8.76	0.34
104		
$CH_2N_2O_3$	2.37	0.62
$CH_4N_4O_2$	2.75	0.43
$C_2H_2NO_4$	2.73	0.83
$C_2H_4N_2O_3$	3.11	0.64
$C_2H_6N_3O_2$	3.48	0.45
$C_2H_8N_4O$	3.85	0.26
$C_3H_4O_4$	3.46	0.84
$C_3H_6NO_3$	3.84	0.66
$C_3H_8N_2O_2$	4.21	0.47
$C_3H_{10}N_3O$	4.59	0.29
$C_3H_{12}N_4$	4.96	0.10
$C_4H_8O_3$	4.57	0.68
$C_4H_{10}NO_2$	4.94	0.50
$C_4H_{12}N_2O$	5.32	0.32
$C_5H_2N_3$	6.58	0.19
$C_5H_{12}O_2$	5.67	0.53
C_6H_2NO	6.94	0.41
$C_6H_4N_2$	7.31	0.23
C_7H_4O	7.67	0.45
C_7H_6N	8.04	0.28
C_8H_8	8.77	0.34
105		
CHN_2O_4	2.02	0.81
$CH_5N_4O_3$	2.39	0.62
$CH_3N_4O_2$	2.77	0.43
$C_2H_5NO_4$	2.75	0.83
$C_2H_7N_2O_3$	3.12	0.64
$C_2H_7N_3O_2$	3.50	0.45
$C_2H_9N_4O$	3.87	0.26
$C_3H_5O_4$	3.48	0.84
$C_3H_7NO_3$	3.85	0.66
$C_3H_9N_2O_2$	4.23	0.47
$C_3H_{11}N_3O$	4.60	0.29
C_4HN_4	5.86	0.15
$C_4H_9O_3$	4.58	0.68
$C_4H_{11}NO_2$	4.96	0.50
C_5HN_2O	6.22	0.36
$C_5H_2N_3$	6.60	0.19
C_6HO_2	6.58	0.58
C_6H_3NO	6.95	0.41
$C_6H_5N_2$	7.33	0.23
C_7H_5O	7.68	0.45
C_7H_7N	8.06	0.28
C_8H_9	8.79	0.34
106		
$CH_2N_2O_4$	2.03	0.82
$CH_4N_4O_3$	2.41	0.62
$CH_6N_4O_2$	2.78	0.43
$C_2H_4NO_4$	2.76	0.83
$C_2H_6N_2O_3$	3.14	0.64
$C_2H_8N_3O_2$	3.51	0.45
$C_2H_{10}N_4O$	3.89	0.26
$C_3H_6O_4$	3.49	0.85
$C_3H_8NO_3$	3.87	0.66
$C_3H_{10}N_2O_2$	4.24	0.47
$C_4H_2N_4$	5.88	0.15
$C_4H_{10}O_3$	4.60	0.68
$C_5H_2N_2O$	6.24	0.36
$C_5H_4N_3$	6.61	0.19
$C_6H_2O_2$	6.59	0.58
C_6H_4NO	6.97	0.41
$C_6H_6N_2$	7.34	0.23
C_7H_6O	7.70	0.46
C_7H_8N	8.07	0.28
C_8H_{10}	8.81	0.34
107		
$CH_3N_2O_4$	2.05	0.82
$CH_5N_4O_3$	2.42	0.62
$CH_7N_4O_2$	2.80	0.43
$C_2H_5NO_4$	2.78	0.83
$C_2H_7N_2O_3$	3.15	0.64
$C_2H_9N_3O_2$	3.53	0.45
$C_2H_{11}N_4O$	3.51	0.85
$C_3H_7O_4$	3.89	0.66
$C_3H_9NO_3$	5.52	0.33
$C_4H_3N_4$	5.90	0.15
C_5HNO_2	5.88	0.54
$C_5H_3N_2O$	6.25	0.37
$C_5H_5N_3$	6.63	0.19
$C_6H_3O_2$	6.61	0.58
C_6H_5NO	6.98	0.41
$C_6H_7N_2$	7.36	0.23
C_7H_7O	7.72	0.46
C_7H_9N	8.09	0.29
C_8H_{11}	8.82	0.34
108		
$CH_4N_2O_4$	2.06	0.82
$CH_6N_4O_3$	2.44	0.62
$CH_8N_4O_2$	2.81	0.43
$C_2H_6NO_4$	2.80	0.83
$C_2H_8N_2O_3$	3.17	0.64
$C_2H_{10}N_3O_2$	3.53	0.85
$C_2H_{12}N_4O$	5.54	0.33
$C_4H_4N_4$	5.91	0.15
$C_5H_2NO_2$	5.90	0.54
$C_5H_4N_2O$	6.27	0.37
$C_5H_6N_3$	6.64	0.19
$C_6H_4O_2$	6.63	0.59
C_6H_6NO	7.00	0.41
$C_6H_8N_2$	7.38	0.24
C_7H_8O	7.73	0.46
$C_7H_{10}N$	8.11	0.29
C_8H_{12}	8.84	0.34
109		
$CH_3N_2O_4$	2.08	0.82
$CH_7N_4O_3$	2.45	0.62
$C_2H_7NO_4$	2.81	0.83
C_3H_9NO	4.82	0.30
$C_4H_5N_4O_2$	5.18	0.51
$C_4H_7N_4O$	5.55	0.33
$C_5H_5N_4$	5.93	0.15
C_5HO_2	5.54	0.73

	P + 1	P + 2
$C_5H_9NO_2$	5.91	0.55
$C_5H_7N_2O$	6.29	0.37
$C_5H_7N_3$	6.66	0.19
$C_6H_8O_3$	6.64	0.59
C_6H_7NO	7.02	0.41
$C_6H_9N_2$	7.39	0.24
C_7H_9O	7.75	0.46
$C_7H_{11}N$	8.12	0.29
C_8H_{13}	8.85	0.35
C_8H	9.74	0.42
110		
$CH_8N_2O_4$	2.10	0.82
$C_3H_2N_4O$	4.84	0.30
$C_4H_2N_2O_2$	5.20	0.51
$C_4H_4N_4O$	5.57	0.33
$C_4H_6N_4$	5.94	0.15
$C_5H_2O_3$	5.55	0.73
$C_5H_4NO_2$	5.93	0.55
$C_5H_6N_2O$	6.30	0.37
$C_5H_8N_3$	6.68	0.19
$C_6H_6O_2$	6.66	0.59
C_6H_8NO	7.03	0.41
$C_6H_{10}N_2$	7.41	0.24
C_7H_6O	7.76	0.46
$C_7H_{12}N$	8.14	0.29
C_8H_4	8.87	0.35
C_8H_2	9.76	0.42
111		
$C_3HN_3O_2$	4.48	0.48
$C_3H_3N_4O$	4.86	0.30
C_4HNO_3	4.84	0.69
$C_4H_3N_2O_2$	5.21	0.51
$C_4H_5N_3O$	5.59	0.33
$C_4H_7N_4$	5.96	0.15
$C_5H_5O_3$	5.57	0.73
$C_5H_5NO_2$	5.94	0.55
$C_5H_7N_2O$	6.32	0.37
$C_5H_9N_3$	6.69	0.19
$C_6H_7O_2$	6.67	0.59
C_6H_9NO	7.05	0.41
$C_6H_{11}N_2$	7.42	0.24
$C_7H_{11}O$	7.78	0.46
$C_7H_{13}N$	8.15	0.29
C_8HN	9.04	0.36
C_8H_{15}	8.89	0.35
C_8H_3	9.77	0.43
112		
$C_3H_4N_4O_2$	4.50	0.48
$C_4H_4N_4O$	4.87	0.30
$C_4H_6NO_3$	4.85	0.70
$C_4H_4N_2O_2$	5.23	0.51
$C_4H_6N_3O$	5.60	0.33
$C_4H_8N_4$	5.98	0.15
$C_5H_4O_3$	5.58	0.73
$C_5H_6NO_2$	5.96	0.55
$C_5H_8N_2O$	6.33	0.37
$C_5H_{10}N_3$	6.71	0.19
$C_6H_8O_2$	6.69	0.59
$C_6H_{10}NO$	7.06	0.41
$C_6H_{12}N_2$	7.44	0.24
$C_7H_{12}O$	7.80	0.46
$C_7H_{14}N$	8.17	0.29
C_8H_2N	9.06	0.36
C_8H_{16}	8.90	0.35
C_8H_4	9.79	0.43
113		
$C_2HN_4O_2$	3.78	0.46
$C_3HN_3O_3$	4.14	0.67
$C_3H_3N_3O_2$	4.51	0.48
$C_3H_5N_3O$	4.89	0.30
C_4HO_4	4.50	0.88
$C_4H_3NO_3$	4.87	0.70
$C_4H_5N_2O_2$	5.24	0.51
$C_4H_7N_3O$	5.62	0.33
$C_4H_9N_4$	5.99	0.15
$C_5H_5O_3$	5.60	0.73
$C_5H_7NO_2$	5.98	0.55
$C_5H_9N_2O$	6.35	0.37
$C_5H_{11}N_3$	6.72	0.19
$C_6H_9O_2$	6.71	0.59
$C_6H_{11}NO$	7.08	0.42
$C_6H_{13}N_2$	7.46	0.24
C_7HN_2	8.34	0.31
$C_7H_{13}O$	7.81	0.46
$C_7H_{15}N$	8.19	0.29
C_8HO	8.70	0.53
C_8H_3N	9.07	0.36
C_8H_{17}	8.92	0.35
C_8H_5	9.81	0.43
114		
$C_2H_2N_4O_2$	3.80	0.46
$C_3H_2N_2O_3$	4.15	0.67
$C_3H_4N_4O_2$	4.53	0.48
$C_3H_6N_4O$	4.90	0.30
$C_4H_2O_4$	4.51	0.88
$C_4H_4NO_3$	4.89	0.70
$C_4H_6N_2O_2$	5.26	0.51
$C_4H_8N_3O$	5.63	0.33
$C_4H_{10}N_4$	6.01	0.15
$C_5H_6O_3$	5.62	0.73
$C_5H_8NO_2$	5.99	0.55
$C_5H_{10}N_2O$	6.37	0.37
$C_5H_{12}N_3$	6.74	0.20
$C_6H_{10}O_2$	6.72	0.59
$C_6H_{12}NO$	7.10	0.42
$C_6H_{14}N_2$	7.47	0.24
$C_7H_2N_2$	8.36	0.31
$C_7H_{14}O$	7.83	0.47
$C_7H_{16}N$	8.20	0.29
C_8H_2O	8.72	0.53
C_8H_4N	9.09	0.37
C_8H_{18}	8.93	0.35
C_8H_6	9.82	0.43
115		
$C_2HN_3O_3$	3.44	0.65
$C_3H_3N_4O_2$	3.81	0.46
C_3HNO_4	3.80	0.86
$C_3H_3N_3O_3$	4.17	0.67
$C_3H_5N_3O_2$	4.54	0.48
$C_3H_7N_4O$	4.92	0.30
$C_4H_3O_4$	4.53	0.88
$C_4H_5NO_3$	4.90	0.70
$C_4H_7N_2O_2$	5.28	0.52
$C_4H_9N_3O$	5.65	0.33
$C_4H_{11}N_4$	6.02	0.16
$C_5H_7O_3$	5.63	0.73
$C_5H_9NO_2$	6.01	0.55
$C_5H_{11}N_2O$	6.38	0.37
$C_5H_{13}N_3$	6.76	0.20
C_6HN_3	7.64	0.25
$C_6H_{11}O_2$	6.74	0.59
$C_6H_{13}NO$	7.11	0.42
$C_6H_{15}N_2$	7.49	0.24
C_7HNO	8.00	0.48
$C_7H_3N_2$	8.38	0.31
$C_7H_{15}O$	7.84	0.47
$C_7H_{17}N$	8.22	0.30
C_8H_3O	8.73	0.54
C_8H_5N	9.11	0.37
C_8H_7	9.84	0.43
116		
$C_2H_2N_2O_3$	3.46	0.65
$C_3H_4N_4O_2$	3.83	0.46
$C_3H_2NO_4$	3.81	0.86
$C_3H_4N_2O_3$	4.19	0.67
$C_3H_6N_2O_2$	4.56	0.49
$C_3H_8N_4O$	4.94	0.30
$C_4H_4O_4$	4.54	0.88
$C_4H_6NO_3$	4.92	0.70
$C_4H_8N_2O_2$	5.29	0.52
$C_4H_{10}N_3O$	5.67	0.34
$C_4H_{12}N_4$	6.04	0.16
$C_5H_6O_3$	5.65	0.73
$C_5H_8NO_2$	6.02	0.55
$C_5H_{10}N_2O$	6.40	0.37
$C_5H_{12}N_3$	6.77	0.20
$C_6H_8N_3$	7.66	0.26
$C_6H_{12}O_2$	6.75	0.59
$C_6H_{14}NO$	7.13	0.42
$C_6H_{16}N_2$	7.50	0.24
C_7H_2NO	8.02	0.48
$C_7H_4N_2$	8.39	0.31
$C_7H_{16}O$	7.86	0.47
C_8H_4O	8.75	0.54
C_8H_6N	9.12	0.37
C_8H_8	9.85	0.43
117		
$C_2HN_2O_4$	3.10	0.84
$C_3H_3N_4O_3$	3.47	0.65
$C_3H_5N_4O_2$	3.85	0.46
$C_3H_7N_4O$	3.83	0.86
$C_3H_5N_2O_3$	4.20	0.67
$C_3H_7N_2O_2$	4.58	0.49
$C_3H_9N_4O$	4.95	0.30
$C_4H_5O_4$	4.56	0.88
$C_4H_7NO_3$	4.93	0.70
$C_4H_9N_2O_2$	5.31	0.52
$C_4H_{11}N_3O$	5.68	0.34
$C_4H_{13}N_4$	6.06	0.16
C_5HN_4	6.95	0.21
$C_5H_9O_3$	5.66	0.73
$C_5H_{11}NO_2$	6.04	0.55
$C_5H_{13}N_2O$	6.41	0.38
$C_5H_{15}N_3$	6.79	0.20
C_6H_9NO	7.30	0.43
$C_6H_{11}N_2$	7.68	0.26
$C_6H_{13}O_2$	6.77	0.60
$C_6H_{15}NO$	7.14	0.42
C_7HO_2	7.66	0.65
C_7H_3NO	8.03	0.48
$C_7H_5N_2$	8.41	0.31
C_8H_5O	8.76	0.54
C_8H_7N	9.14	0.37
C_8H_9	9.87	0.43
118		
$C_2H_2N_2O_4$	3.11	0.84
$C_3H_4N_4O_3$	3.49	0.65
$C_3H_6N_4O_2$	3.86	0.46
$C_3H_8N_4O$	3.84	0.86
$C_3H_6N_2O_3$	4.22	0.67
$C_3H_8N_2O_2$	4.59	0.49
$C_3H_{10}N_4O$	4.97	0.30
$C_4H_6O_4$	4.58	0.88
$C_4H_8NO_3$	4.95	0.70
$C_4H_{10}N_2O_2$	5.32	0 52
$C_4H_{12}N_3O$	5.70	0.34
$C_4H_{14}N_4$	6.07	0.16
$C_5H_8N_4$	6.96	0.21
$C_5H_{10}O_3$	5.68	0.73
$C_5H_{12}NO_2$	6.06	0.55
$C_5H_{14}N_2O$	6.43	0.38
$C_6H_{12}N_2O$	7.32	0.43
$C_6H_4N_2$	7.69	0.26
$C_6H_{14}O_2$	6.79	0.60
$C_7H_2O_2$	7.67	0.65
C_7H_4NO	8.05	0.48
$C_7H_6N_2$	8.42	0.31
C_8H_6O	8.78	0.54
C_8H_8N	9.15	0.37
C_8H_{10}	9.89	0.44
119		
$C_2H_3N_2O_4$	3.13	0.84
$C_3H_5N_4O_3$	3.50	0.65
$C_3H_7N_4O_2$	3.88	0.46
$C_3H_9NO_4$	3.86	0.86
$C_3H_7N_2O_3$	4.23	0.67
$C_3H_9N_4O_2$	4.61	0.49
$C_3H_{11}N_4O$	4.98	0.30
$C_4H_7O_4$	4.59	0.88
$C_4H_9NO_3$	4.97	0.70
$C_4H_{11}N_2O_2$	5.34	0.52
$C_4H_{13}N_3O$	5.71	0.34
C_5H_9NO	6.60	0.39
$C_5H_{11}N_4$	6.98	0.21
$C_5H_{11}O_3$	5.70	0.73
$C_5H_{13}NO_2$	6.07	0.56
C_6HNO_2	6.96	0.61
$C_6H_3N_2O$	7.33	0.43
$C_6H_5N_3$	7.71	0.26
$C_6H_{13}O_2$	7.69	0.66
C_7H_9NO	8.07	0.48
$C_7H_{11}N_2$	8.44	0.31
C_8H_9O	8.80	0.54
$C_8H_{11}N$	9.17	0.37
C_8H_{11}	9.90	0.44

	P + 1	P + 2
120		
$C_5H_4N_2O_4$	3.15	0.84
$C_5H_6N_3O_3$	3.52	0.65
$C_5H_8N_4O_2$	3.89	0.46
$C_5H_{12}NO_4$	3.88	0.86
$C_5H_9N_2O_3$	4.25	0.67
$C_5H_{16}N_3O_2$	4.62	0.49
$C_5H_{12}N_4O$	5.00	0.31
C_4HF_4O	4.61	0.88
$C_4H_{12}NO_3$	4.98	0.70
$C_4H_{12}N_2O_2$	5.36	0.52
$C_5H_9N_2O$	6.62	0.39
$C_9H_4N_4$	6.99	0.21
$C_5H_{12}O_3$	5.71	0.74
$C_5H_7NO_3$	6.98	0.61
$C_5H_9N_2O$	7.35	0.43
$C_9H_6N_3$	7.72	0.26
$C_7H_4O_2$	7.71	0.66
C_7H_6NO	8.08	0.49
$C_7H_8N_2$	8.46	0.32
C_9H_8O	8.81	0.54
$C_9H_{10}N$	9.19	0.37
C_9H_{12}	9.92	0.44
121		
$C_5H_5N_2O_4$	3.16	0.84
$C_5H_7N_3O_3$	3.54	0.65
$C_5H_9N_4O_2$	3.91	0.46
$C_5H_7NO_4$	3.89	0.86
$C_5H_9N_2O_3$	4.27	0.67
$C_5H_{11}N_3O_2$	4.64	0.49
C_5HNO	5.90	0.35
$C_4H_5O_4$	4.62	0.89
$C_4H_{11}NO_3$	5.00	0.70
$C_5HN_2O_3$	6.26	0.57
$C_5H_5N_2O$	6.64	0.39
$C_5H_7N_4$	7.01	0.21
C_6HO_3	6.62	0.79
$C_6H_5NO_3$	6.99	0.61
$C_6H_7N_2O$	7.37	0.44
$C_6H_7N_3$	7.74	0.26
$C_7H_5O_2$	7.72	0.66
C_7H_7NO	8.10	0.49
$C_7H_9N_2$	8.47	0.32
C_9H_6O	8.83	0.54
$C_9H_{11}N$	9.20	0.38
C_9H_{13}	9.93	0.44
$C_{10}H$	10.82	0.53
122		
$C_5H_6N_2O_4$	3.18	0.84
$C_5H_8N_3O_3$	3.55	0.65
$C_5H_{10}N_4O_2$	3.93	0.46
$C_5H_9NO_4$	3.91	0.86
$C_5H_{11}N_2O_3$	4.28	0.67
$C_4H_6N_4O$	5.92	0.35
$C_4H_{10}O_4$	4.64	0.89
$C_5H_2N_2O_2$	6.28	0.57
$C_5H_4N_2O$	6.65	0.39
$C_5H_6N_4$	7.03	0.21
$C_6H_2O_3$	6.63	0.79
$C_6H_4NO_2$	7.01	0.61
$C_6H_6N_2O$	7.38	0.44
$C_6H_8N_3$	7.76	0.26
$C_7H_6O_2$	7.74	0.66
C_7H_8NO	8.11	0.49
$C_7H_{10}N_2$	8.49	0.32
$C_8H_{10}O$	8.84	0.54
$C_8H_{12}N$	9.22	0.38
C_8H_{14}	9.95	0.44
$C_{10}H_2$	10.84	0.53
123		
$C_7H_7N_2O_4$	3.19	0.84
$C_5H_9N_3O_3$	3.57	0.65
$C_5H_{11}NO_4$	3.92	0.86
$C_4HN_3O_2$	5.56	0.53
$C_4H_3N_4O$	5.94	0.35
C_5HNO_3	5.92	0.75
$C_5H_5N_2O_2$	6.29	0.57
$C_5H_7N_3O$	6.67	0.39
$C_5H_7N_4$	7.04	0.22
$C_6H_3O_3$	6.65	0.79
$C_6H_5NO_3$	7.02	0.61
$C_6H_7N_2O$	7.40	0.44
$C_6H_9N_3$	7.77	0.26
$C_7H_7O_2$	7.75	0.66
C_7H_9NO	8.13	0.49
$C_7H_{11}N_2$	8.50	0.32
$C_8H_{11}O$	8.86	0.55
$C_8H_{13}N$	9.23	0.38
C_8HN	10.12	0.46
C_8H_{15}	9.97	0.44
$C_{10}H_3$	10.85	0.53
124		
$C_7H_8N_2O_4$	3.21	0.84
$C_6H_2N_3O_2$	5.58	0.53
$C_6H_4N_4O$	5.95	0.35
$C_5H_2NO_3$	5.93	0.75
$C_5H_4N_2O_2$	6.31	0.57
$C_5H_6N_3O$	6.68	0.39
$C_5H_8N_4$	7.06	0.22
$C_6H_4O_3$	6.67	0.79
$C_6H_6NO_2$	7.04	0.61
$C_6H_8N_2O$	7.41	0.44
$C_6H_{10}N_3$	7.79	0.27
$C_7H_8O_2$	7.77	0.66
$C_7H_{10}NO$	8.15	0.49
$C_7H_{12}N_2$	8.52	0.32
$C_8H_{12}O$	8.88	0.55
$C_8H_{14}N$	9.25	0.38
C_8H_2N	10.14	0.46
C_8H_{16}	9.98	0.45
$C_{10}H_4$	10.87	0.53
125		
$C_5HN_4O_3$	4.86	0.50
$C_4HN_5O_3$	5.22	0.71
$C_4H_3N_4O_2$	5.59	0.53
$C_4H_5N_4O$	5.97	0.35
C_5HO_4	5.58	0.93
$C_5H_3NO_3$	5.95	0.75
$C_5H_5N_2O_2$	6.32	0.57
$C_5H_7N_3O$	6.70	0.39
$C_5H_9N_4$	7.07	0.22
$C_6H_5O_3$	6.68	0.79
$C_6H_7NO_2$	7.06	0.61
$C_6H_9N_2O$	7.43	0.44
$C_6H_{11}N_3$	7.80	0.27
$C_7H_9O_2$	7.79	0.66
$C_7H_{11}NO$	8.16	0.49
$C_7H_{13}N_2$	8.54	0.32
C_9HN_2	9.42	0.40
$C_9H_{13}O$	8.89	0.55
$C_9H_{15}N$	9.27	0.38
C_9HO	9.78	0.63
C_9H_3N	10.16	0.46
C_9H_{17}	10.00	0.45
$C_{10}H_5$	10.89	0.53
126		
$C_5H_2N_4O_2$	4.88	0.50
$C_4H_2N_5O_3$	5.24	0.71
$C_4H_4N_5O_2$	5.61	0.53
$C_4H_6N_5O$	5.98	0.35
$C_5H_3O_4$	5.59	0.93
$C_5H_4NO_3$	5.97	0.75
$C_5H_6N_3O_2$	6.34	0.57
$C_5H_8N_3O$	6.72	0.35
$C_5H_{10}N_4$	7.09	0.22
$C_6H_6O_3$	6.70	0.79
$C_6H_8NO_2$	7.07	0.62
$C_6H_{10}N_2O$	7.45	0.44
$C_6H_{12}N_3$	7.82	0.27
$C_7H_{10}O_2$	7.80	0.66
$C_7H_{12}NO$	8.18	0.49
$C_7H_{14}N_2$	8.55	0.32
$C_9H_2N_2$	9.44	0.40
$C_9H_{14}O$	8.91	0.55
$C_9H_{16}N$	9.28	0.38
C_9HO	9.80	0.63
C_9H_4N	10.17	0.46
C_9H_{18}	10.01	0.45
$C_{10}H_6$	10.90	0.54
127		
$C_5HN_3O_3$	4.52	0.68
$C_5H_3N_4O_2$	4.89	0.50
C_4HNO_4	4.88	0.90
$C_4H_3N_5O_3$	5.25	0.71
$C_4H_5N_5O_2$	5.63	0.53
$C_4H_7N_4O$	6.00	0.35
$C_5H_3O_4$	5.61	0.93
$C_5H_5NO_3$	5.98	0.75
$C_5H_7N_2O_2$	6.36	0.57
$C_5H_9N_3O$	6.73	0.40
$C_5H_{11}N_4$	7.11	0.22
$C_6H_7O_3$	6.71	0.79
$C_6H_9NO_2$	7.09	0.62
$C_6H_{11}N_2O$	7.46	0.44
$C_6H_{13}N_3$	7.84	0.27
C_7HN_3	8.73	0.34
$C_7H_{11}O_2$	7.82	0.67
$C_7H_{13}NO$	8.19	0.49
$C_7H_{15}N_2$	8.57	0.32
C_8HNO	9.08	0.57
$C_8H_3N_2$	9.46	0.40
$C_8H_{15}O$	8.92	0.55
$C_8H_{17}N$	9.30	0.38
C_8H_3O	9.81	0.63
C_8H_5N	10.19	0.47
C_8H_{17}	10.03	0.45
$C_{10}H_7$	10.92	0.54
128		
$C_5H_2N_3O_3$	4.54	0.68
$C_5H_4N_4O_2$	4.91	0.50
$C_4H_2NO_4$	4.89	0.90
$C_4H_4N_5O_3$	5.27	0.72
$C_4H_6N_5O_2$	5.64	0.53
$C_4H_8N_4O$	6.02	0.36
$C_5H_4O_4$	5.62	0.93
$C_5H_6NO_3$	6.00	0.75
$C_5H_8N_2O_2$	6.37	0.57
$C_5H_{10}N_3O$	6.75	0.40
$C_5H_{12}N_4$	7.12	0.22
$C_6H_8O_3$	6.73	0.79
$C_6H_{10}NO_2$	7.10	0.62
$C_6H_{12}N_2O$	7.48	0.44
$C_6H_{14}N_3$	7.85	0.27
$C_7H_2N_3$	8.74	0.34
$C_7H_{12}O_2$	7.83	0.67
$C_7H_{14}NO$	8.21	0.50
$C_7H_{16}N_2$	8.58	0.33
C_8H_2NO	9.10	0.57
$C_8H_4N_2$	9.47	0.40
$C_8H_{16}O$	8.94	0.55
$C_8H_{18}N$	9.31	0.39
C_8H_4O	9.83	0.63
C_8H_6N	10.20	0.47
C_8H_{18}	10.05	0.45
$C_{10}H_8$	10.94	0.54
129		
$C_5HN_2O_4$	4.18	0.87
$C_5H_3N_3O_3$	4.55	0.69
$C_5H_5N_4O_2$	4.93	0.50
$C_5H_9NO_4$	4.91	0.90
$C_5H_7N_2O_3$	5.28	0.72
$C_5H_7N_3O_2$	5.66	0.54
$C_5H_9N_4O$	6.03	0.36
$C_5H_5O_4$	5.64	0.93
$C_5H_7NO_3$	6.01	0.75
$C_5H_9N_2O_2$	6.39	0.57
$C_5H_{11}N_3O$	6.76	0.40
$C_5H_{13}N_4$	7.14	0.22
C_6HN_4	8.03	0.28
$C_6H_9O_3$	6.75	0.79
$C_6H_{11}NO_2$	7.12	0.62
$C_6H_{13}N_2O$	7.49	0.44
$C_6H_{15}N_3$	7.87	0.27
C_7HN_2O	8.38	0.51
$C_7H_3N_3$	8.76	0.34
$C_7H_{13}O_2$	7.85	0.67
$C_7H_{15}NO$	8.23	0.50
$C_7H_{17}N_2$	8.60	0.33
C_8HO_2	8.74	0.74
C_8H_3NO	9.11	0.57
$C_8H_5N_2$	9.49	0.40
$C_8H_{17}O$	8.96	0.55
$C_8H_{19}N$	9.33	0.39
C_8H_5O	9.85	0.63
C_8H_7N	10.22	0.47
$C_{10}H_9$	10.95	0.54

	P + 1	P + 2
130		
$C_5H_2N_2O_4$	4.19	0.87
$C_5H_4N_2O_3$	4.57	0.69
$C_5H_6N_4O_2$	4.94	0.50
$C_4H_6NO_4$	4.92	0.90
$C_4H_8N_2O_3$	5.30	0.72
$C_4H_8N_2O_3$	5.67	0.54
$C_4H_{10}N_4O$	6.05	0.36
$C_5H_6O_4$	5.66	0.93
$C_5H_9NO_3$	6.03	0.75
$C_5H_{10}N_2O_2$	6.40	0.58
$C_5H_{12}N_2O$	6.78	0.40
$C_5H_{14}N_4$	7.15	0.22
$C_6H_8N_4$	8.04	0.29
$C_6H_{10}O_3$	6.76	0.79
$C_6H_{12}NO_2$	7.14	0.62
$C_6H_{14}N_2O$	7.51	0.45
$C_6H_{16}N_3$	7.88	0.27
$C_7H_8N_2O$	8.40	0.51
$C_7H_4N_3$	8.77	0.34
$C_7H_{14}O_2$	7.87	0.67
$C_7H_{16}NO$	8.24	0.50
$C_7H_{18}N_2$	8.62	0.33
$C_8H_8O_2$	8.76	0.74
C_8H_9NO	9.13	0.57
$C_8H_{10}N_2$	9.50	0.40
$C_8H_{12}O$	8.97	0.56
$C_8H_{14}O$	9.86	0.63
$C_8H_{15}N$	10.24	0.47
$C_{10}H_{10}$	10.97	0.54
131		
$C_3H_3N_2O_4$	4.21	0.87
$C_3H_5N_2O_3$	4.58	0.69
$C_3H_7N_4O_2$	4.96	0.50
$C_4H_5NO_4$	4.94	0.90
$C_4H_7N_2O_3$	5.32	0.72
$C_4H_9N_2O_2$	5.69	0.54
$C_4H_{11}N_4O$	6.06	0.36
$C_5H_7O_4$	5.67	0.93
$C_5H_9NO_3$	6.05	0.75
$C_5H_{11}N_2O_2$	6.42	0.58
$C_5H_{13}N_2O$	6.80	0.40
$C_5H_{15}N_4$	7.17	0.22
C_6HN_3O	7.68	0.46
$C_6H_3N_4$	8.06	0.29
$C_6H_{11}O_3$	6.78	0.80
$C_6H_{13}NO_2$	7.15	0.62
$C_6H_{15}N_2O$	7.53	0.45
$C_6H_{17}N_3$	7.90	0.27
C_7HNO_2	8.04	0.68
$C_7H_3N_2O$	8.41	0.51
$C_7H_5N_3$	8.79	0.34
$C_7H_{13}O_2$	7.88	0.67
$C_7H_{17}NO$	8.26	0.50
$C_8H_3O_2$	8.77	0.74
C_8H_5NO	9.15	0.57
$C_8H_7N_2$	9.52	0.41
C_8H_7O	9.88	0.64
C_8H_9N	10.25	0.47
$C_{10}H_{11}$	10.98	0.54
132		
$C_3H_4N_2O_4$	4.23	0.87
$C_3H_6N_2O_3$	4.60	0.69
$C_3H_8N_4O_2$	4.97	0.50
$C_4H_8NO_4$	4.96	0.90
$C_4H_8N_2O_3$	5.33	0.72
$C_4H_{10}N_2O_2$	5.71	0.54
$C_4H_{12}N_4O$	6.08	0.36
$C_5H_8O_4$	5.69	0.93
$C_5H_{10}NO_3$	6.06	0.76
$C_5H_{12}N_2O_2$	6.44	0.58
$C_5H_{14}N_2O$	6.81	0.40
$C_5H_{16}N_4$	7.19	0.23
$C_6H_2N_2O$	7.70	0.46
$C_6H_4N_4$	8.07	0.29
$C_6H_{12}O_3$	6.97	0.80
$C_6H_{14}NO_2$	7.17	0.62
$C_6H_{16}N_2O$	7.54	0.45
$C_7H_2NO_2$	8.06	0.68
$C_7H_4N_2O$	8.43	0.51
$C_7H_6N_3$	8.81	0.34
$C_7H_{18}O_2$	7.90	0.67
$C_8H_4O_2$	8.79	0.74
C_8H_6NO	9.16	0.57
$C_8H_8N_2$	9.54	0.41
C_8H_8O	9.89	0.64
$C_9H_{12}N$	10.27	0.47
$C_{10}H_{12}$	11.00	0.55
133		
$C_3H_5N_2O_4$	4.24	0.87
$C_3H_7N_2O_3$	4.62	0.69
$C_3H_9N_4O_2$	4.99	0.51
$C_4H_7NO_4$	4.97	0.90
$C_4H_9N_2O_3$	5.35	0.72
$C_4H_{11}N_2O_2$	5.72	0.54
$C_4H_{13}N_4O$	6.10	0.36
C_5H_9NO	6.98	0.41
$C_5H_9O_4$	5.70	0.94
$C_5H_{11}NO_3$	6.08	0.76
$C_5H_{13}N_2O_2$	6.45	0.58
$C_5H_{15}N_2O$	6.83	0.40
$C_6HN_2O_2$	7.34	0.63
$C_6H_3N_3O$	7.72	0.46
$C_6H_5N_4$	8.09	0.29
$C_6H_{13}O_3$	6.81	0.80
$C_6H_{15}NO_2$	7.18	0.62
C_7HO_3	7.70	0.86
$C_7H_3NO_2$	8.07	0.69
$C_7H_5N_2O$	8.45	0.51
$C_7H_7N_3$	8.82	0.35
$C_8H_5O_2$	8.80	0.74
C_8H_7NO	9.18	0.57
$C_8H_9N_2$	9.55	0.41
C_8H_9O	9.91	0.64
$C_9H_{11}N$	10.28	0.48
$C_{10}H_{13}$	11.01	0.55
$C_{11}H$	11.90	0.64
134		
$C_3H_6N_2O_4$	4.26	0.87
$C_3H_8N_2O_3$	4.63	0.69
$C_3H_{10}N_4O_2$	5.01	0.51
$C_4H_8NO_4$	4.99	0.90
$C_4H_{10}N_2O_3$	5.36	0.72
$C_4H_{12}N_2O_2$	5.74	0.54
$C_4H_{14}N_4O$	6.11	0.36
$C_5H_8N_4O$	7.00	0.41
$C_5H_{10}O_4$	5.72	0.94
$C_5H_{12}NO_3$	6.09	0.76
$C_5H_{14}N_2O_2$	6.47	0.58
$C_6H_2N_2O_2$	7.36	0.64
$C_6H_4N_2O$	7.73	0.46
$C_6H_6N_4$	8.11	0.29
$C_6H_{14}O_3$	6.83	0.80
$C_7H_4O_3$	7.71	0.86
$C_7H_6NO_2$	8.09	0.69
$C_7H_8N_2O$	8.46	0.52
$C_7H_8N_3$	8.84	0.35
$C_8H_8O_2$	8.82	0.74
C_8H_9NO	9.19	0.58
$C_8H_{10}N_2$	9.57	0.41
$C_8H_{10}O$	9.93	0.64
$C_9H_{12}N$	10.30	0.48
$C_{10}H_{14}$	11.03	0.55
$C_{11}H_2$	11.92	0.65
135		
$C_3H_7N_2O_4$	4.27	0.87
$C_3H_9N_2O_3$	4.65	0.69
$C_3H_{11}N_4O_2$	5.02	0.51
$C_4H_9NO_4$	5.00	0.90
$C_4H_{11}N_2O_3$	5.38	0.72
$C_4H_{13}N_2O_2$	5.75	0.54
$C_5HN_2O_2$	6.64	0.59
$C_5H_3N_4O$	7.02	0.41
$C_5H_{11}O_4$	5.74	0.94
$C_5H_{13}NO_3$	6.11	0.76
C_6HNO_3	7.00	0.81
$C_6H_3N_2O_2$	7.37	0.64
$C_6H_5N_3O$	7.75	0.46
$C_6H_7N_4$	8.12	0.29
$C_7H_5O_3$	7.73	0.86
$C_7H_7NO_2$	8.10	0.69
$C_7H_9N_2O$	8.48	0.52
$C_7H_9N_3$	8.85	0.35
$C_8H_9O_2$	8.84	0.74
$C_8H_{11}NO$	9.21	0.58
$C_8H_{11}N_2$	9.58	0.41
$C_8H_{11}O$	9.94	0.64
$C_9H_{13}N$	10.32	0.48
$C_{10}HN$	11.20	0.57
$C_{10}H_{15}$	11.05	0.55
$C_{11}H_3$	11.94	0.65
136		
$C_3H_8N_2O_4$	4.29	0.87
$C_3H_{10}N_2O_3$	4.66	0.69
$C_3H_{12}N_4O_2$	5.04	0.51
$C_4H_{10}NO_4$	5.02	0.90
$C_4H_{12}N_2O_3$	5.40	0.72
$C_5H_2N_2O_2$	6.66	0.59
$C_5H_4N_4O$	7.03	0.42
$C_5H_{12}O_4$	5.75	0.94
$C_6H_2NO_3$	7.01	0.81
$C_6H_4N_2O_2$	7.39	0.64
$C_6H_6N_2O$	7.76	0.46
$C_6H_8N_4$	8.14	0.29
$C_7H_4O_3$	7.75	0.86
$C_7H_6NO_2$	8.12	0.69
$C_7H_8N_2O$	8.49	0.52
$C_7H_{10}N_3$	8.87	0.35
$C_8H_8O_2$	8.85	0.75
$C_8H_{10}NO$	9.23	0.58
$C_8H_{12}N_2$	9.60	0.41
$C_8H_{12}O$	9.96	0.64
$C_8H_{14}N$	10.33	0.48
$C_{10}H_2N$	11.22	0.57
$C_{10}H_{18}$	11.06	0.55
$C_{11}H_4$	11.95	0.65
137		
$C_3H_9N_2O_4$	4.31	0.88
$C_3H_{11}N_2O_3$	4.68	0.69
$C_4HN_4O_2$	5.94	0.55
$C_4H_{11}NO_4$	5.04	0.90
$C_4HN_2O_3$	6.30	0.77
$C_4H_3N_2O_2$	6.67	0.59
$C_5H_5N_4O$	7.05	0.42
C_6HO_4	6.66	0.99
$C_6H_3NO_3$	7.03	0.81
$C_6H_5N_2O_2$	7.41	0.64
$C_6H_7N_2O$	7.78	0.47
$C_6H_9N_4$	8.15	0.29
$C_7H_5O_3$	7.76	0.86
$C_7H_7NO_2$	8.14	0.69
$C_7H_9N_2O$	8.51	0.52
$C_7H_{11}N_3$	8.89	0.35
$C_8H_9O_2$	8.87	0.75
$C_8H_{11}NO$	9.24	0.58
$C_8H_{13}N_2$	9.62	0.41
C_8HN_2	10.50	0.50
$C_8H_{13}O$	9.97	0.65
$C_8H_{15}N$	10.35	0.48
$C_{10}HO$	10.86	0.73
$C_{10}H_3N$	11.24	0.57
$C_{10}H_{17}$	11.08	0.56
$C_{11}H_5$	11.97	0.65
138		
$C_3H_{10}N_2O_4$	4.32	0.88
$C_4H_2N_4O_2$	5.96	0.55
$C_5H_2N_2O_3$	6.32	0.77
$C_5H_4N_3O_2$	6.69	0.59
$C_5H_6N_4O$	7.06	0.42
$C_6H_2O_4$	6.67	0.99
$C_6H_4NO_3$	7.05	0.81
$C_6H_6N_2O_2$	7.42	0.64
$C_6H_8N_3O$	7.80	0.47
$C_6H_{10}N_4$	8.17	0.30
$C_7H_6O_3$	7.78	0.86
$C_7H_8NO_2$	8.15	0.69
$C_7H_{10}N_2O$	8.53	0.52
$C_7H_{12}N_3$	8.90	0.35
$C_8H_{10}O_2$	8.88	0.75
$C_8H_{12}NO$	9.26	0.58
$C_8H_{14}N_2$	9.63	0.42
$C_8H_2N_2$	10.52	0.50
$C_8H_{14}O$	9.99	0.65
$C_8H_{16}N$	10.36	0.48
$C_{10}H_2O$	10.88	0.73

	P + 1	P + 2
$C_{10}H_4N$	11.25	0.57
$C_{10}H_{18}$	11.09	0.56
$C_{11}H_6$	11.98	0.65
139		
$C_4H_9N_2O_3$	5.60	0.73
$C_4H_3N_4O_2$	5.97	0.55
C_5HNO_4	5.96	0.95
$C_5H_5N_2O_2$	6.33	0.77
$C_5H_7N_2O_2$	6.71	0.59
$C_5H_7N_2O$	7.03	0.42
$C_6H_9O_4$	6.69	0.99
$C_6H_5NO_2$	7.06	0.82
$C_6H_7N_2O_2$	7.44	0.64
$C_6H_9N_2O$	7.81	0.47
$C_6H_{11}N_4$	8.19	0.30
$C_7H_7O_3$	7.79	0.86
$C_7H_9NO_2$	8.17	0.69
$C_7H_{11}N_2O$	8.54	0.52
$C_7H_{13}N_2$	8.92	0.35
C_8HN_3	9.81	0.43
$C_8H_{11}O_2$	8.90	0.75
$C_8H_{13}NO$	9.27	0.58
$C_8H_{15}N_2$	9.65	0.42
C_8HNO	10.16	0.66
$C_8H_3N_2$	10.54	0.50
$C_8H_{15}O$	10.01	0.65
$C_8H_{17}N$	10.38	0.49
$C_{10}H_9O$	10.89	0.74
$C_{10}H_5N$	11.27	0.58
$C_{10}H_{13}$	11.11	0.56
$C_{11}H_7$	12.00	0.66
140		
$C_4H_2N_2O_3$	5.62	0.73
$C_4H_4N_4O_2$	5.99	0.55
$C_5H_2NO_4$	5.97	0.95
$C_5H_4N_2O_3$	6.35	0.77
$C_5H_6N_2O_2$	6.72	0.60
$C_5H_8N_4O$	7.10	0.42
$C_6H_4O_4$	6.70	0.99
$C_6H_6NO_3$	7.08	0.82
$C_6H_8N_2O_2$	7.45	0.64
$C_6H_{10}N_3O$	7.83	0.47
$C_6H_{12}N_4$	8.20	0.30
$C_7H_8O_3$	7.81	0.87
$C_7H_{10}NO_2$	8.18	0.69
$C_7H_{12}N_2O$	8.56	0.52
$C_7H_{14}N_2$	8.93	0.36
$C_8H_2N_3$	9.82	0.43
$C_8H_{12}O_2$	8.92	0.75
$C_8H_{14}NO$	9.29	0.58
$C_8H_{16}N_2$	9.66	0.42
C_9H_5NO	10.18	0.67
$C_9H_9N_2$	10.55	0.50
$C_9H_{16}O$	10.02	0.65
$C_9H_{18}N$	10.40	0.49
$C_{10}H_4O$	10.91	0.74
$C_{10}H_8N$	11.28	0.58
$C_{10}H_{20}$	11.13	0.56
$C_{11}H_8$	12.02	0.66
141		
$C_4HN_2O_4$	5.26	0.92
$C_4H_9N_3O_3$	5.63	0.73
$C_4H_5N_4O_2$	6.01	0.56
$C_5H_3NO_4$	5.99	0.95
$C_5H_5N_2O_3$	6.36	0.77
$C_5H_7N_2O_2$	6.74	0.60
$C_5H_9N_4O$	7.11	0.42
$C_6H_5O_4$	6.72	0.99
$C_6H_7NO_3$	7.09	0.82
$C_6H_9N_2O_2$	7.47	0.64
$C_6H_{11}N_2O$	7.84	0.47
$C_6H_{13}N_4$	8.22	0.30
C_7HN_4	9.11	0.37
$C_7H_9O_3$	7.83	0.87
$C_7H_{11}NO_2$	8.20	0.70
$C_7H_{13}N_2O$	8.57	0.53
$C_7H_{15}N_2$	8.95	0.36
$C_8H_3NO_2$	9.46	0.60
$C_8H_3N_3$	9.84	0.44
$C_8H_{13}O_2$	8.93	0.75
$C_8H_{15}NO$	9.31	0.59
$C_8H_{17}N_2$	9.68	0.42
C_9HO_2	9.82	0.83
C_9H_9NO	10.19	0.67
$C_9H_{11}N_2$	10.57	0.50
$C_9H_{17}O$	10.04	0.65
$C_9H_{19}N$	10.41	0.49
$C_{10}H_5O$	10.93	0.74
$C_{10}H_7N$	11.30	0.58
$C_{10}H_{21}$	11.14	0.56
$C_{11}H_9$	12.03	0.66
142		
$C_4H_2N_2O_4$	5.27	0.92
$C_4H_4N_2O_3$	5.65	0.74
$C_5H_2N_4O_2$	6.02	0.56
$C_5H_4NO_4$	6.01	0.95
$C_5H_6N_2O_3$	6.38	0.77
$C_5H_8N_2O_2$	6.75	0.60
$C_5H_{10}N_4O$	7.13	0.42
$C_6H_6O_4$	6.74	0.99
$C_6H_8NO_3$	7.11	0.82
$C_6H_{10}N_2O_2$	7.49	0.64
$C_6H_{12}N_2O$	7.86	0.47
$C_6H_{14}N_4$	8.23	0.30
$C_7H_2N_4$	9.12	0.37
$C_7H_{10}O_3$	7.84	0.87
$C_7H_{12}NO_2$	8.22	0.70
$C_7H_{14}N_2O$	8.59	0.53
$C_7H_{16}N_2$	8.97	0.36
$C_8H_2N_2O$	9.48	0.60
$C_8H_4N_3$	9.85	0.44
$C_8H_{14}O_2$	8.95	0.75
$C_8H_{16}NO$	9.32	0.59
$C_8H_{18}N_2$	9.70	0.42
$C_9H_5O_2$	9.84	0.83
$C_9H_{11}NO$	10.21	0.67
$C_9H_{13}N_2$	10.58	0.51
$C_9H_{19}O$	10.05	0.65
$C_9H_{21}N$	10.43	0.49
$C_{10}H_6O$	10.94	0.74
$C_{10}H_8N$	11.32	0.58
$C_{10}H_{22}$	11.16	0.56
$C_{11}H_{10}$	12.05	0.66
143		
$C_4H_9N_2O_4$	5.29	0.92
$C_4H_5N_4O_3$	5.66	0.74
$C_4H_7N_4O_2$	6.04	0.56
$C_5H_5NO_4$	6.02	0.95
$C_5H_7N_2O_3$	6.40	0.78
$C_5H_9N_2O_2$	6.77	0.60
$C_5H_{11}N_4O$	7.14	0.42
$C_6H_7O_4$	6.75	0.99
$C_6H_9NO_3$	7.13	0.82
$C_6H_{11}N_2O_2$	7.50	0.65
$C_6H_{13}N_2O$	7.88	0.47
$C_6H_{15}N_4$	8.25	0.30
C_7HN_2O	8.76	0.54
$C_7H_3N_4$	9.14	0.37
$C_7H_{11}O_3$	7.86	0.87
$C_7H_{13}NO_2$	8.23	0.70
$C_7H_{15}N_2O$	8.61	0.53
$C_7H_{17}N_2$	8.98	0.36
C_8HNO_2	9.12	0.77
$C_8H_3N_2O$	9.50	0.60
$C_8H_5N_3$	9.87	0.44
$C_8H_{15}O_2$	8.96	0.76
$C_8H_{17}NO$	9.34	0.59
$C_8H_{19}N_2$	9.71	0.42
$C_9H_3O_2$	9.85	0.83
C_9H_5NO	10.23	0.67
$C_9H_7N_2$	10.60	0.51
$C_9H_{13}O$	10.07	0.65
$C_9H_{21}N$	10.44	0.49
$C_{10}H_7O$	10.96	0.74
$C_{10}H_9N$	11.33	0.58
$C_{11}H_{11}$	12.06	0.66
144		
$C_4H_4N_2O_4$	5.31	0.92
$C_4H_6N_2O_3$	5.68	0.74
$C_4H_8N_2O_2$	6.05	0.56
$C_5H_6NO_4$	6.04	0.95
$C_5H_8N_2O_3$	6.41	0.78
$C_5H_{10}N_2O_2$	6.79	0.60
$C_5H_{12}N_4O$	7.16	0.42
$C_6H_8O_4$	6.77	1.00
$C_6H_{10}NO_3$	7.14	0.82
$C_6H_{12}N_2O_2$	7.52	0.65
$C_6H_{14}N_2O$	7.89	0.47
$C_6H_{16}N_4$	8.27	0.30
$C_7H_2N_2O$	8.78	0.54
$C_7H_4N_3$	9.15	0.38
$C_7H_{12}O_3$	7.87	0.87
$C_7H_{14}NO_2$	8.25	0.70
$C_7H_{16}N_2O$	8.62	0.53
$C_7H_{18}N_2$	9.00	0.36
$C_8H_4N_2O$	9.14	0.77
$C_8H_6N_3$	9.51	0.60
$C_8H_{16}O_2$	8.98	0.76
$C_8H_{18}NO$	9.35	0.59
$C_8H_{20}N_2$	9.73	0.43
$C_9H_8O_2$	9.87	0.84
$C_9H_{10}NO$	10.24	0.67
$C_9H_{12}N_2$	10.62	0.51
$C_9H_{20}O$	10.09	0.66
$C_{10}H_8O$	10.97	0.74
$C_{10}H_{10}N$	11.35	0.58
$C_{11}H_{12}$	12.08	0.67
145		
$C_4H_5N_2O_4$	5.32	0.92
$C_4H_7N_2O_3$	5.70	0.74
$C_4H_9N_4O_2$	6.07	0.56
$C_5H_7NO_4$	6.05	0.96
$C_5H_9N_2O_3$	6.43	0.78
$C_5H_{11}N_2O_2$	6.80	0.60
$C_5H_{13}N_4O$	7.18	0.43
C_6HN_4O	8.07	0.49
$C_6H_9O_4$	6.78	1.00
$C_6H_{11}NO_3$	7.16	0.82
$C_6H_{13}N_2O_2$	7.53	0.65
$C_6H_{15}N_2O$	7.91	0.48
$C_6H_{17}N_4$	8.28	0.31
$C_7HN_2O_2$	8.42	0.71
$C_7H_9N_2O$	8.80	0.54
$C_7H_5N_4$	9.17	0.38
$C_7H_{13}O_3$	7.89	0.87
$C_7H_{15}NO_2$	8.26	0.70
$C_7H_{17}N_2O$	8.64	0.53
$C_7H_{19}N_2$	9.01	0.36
C_8HO_3	8.78	0.94
$C_8H_9NO_2$	9.15	0.77
$C_8H_{11}N_2O$	9.53	0.61
$C_8H_7N_3$	9.90	0.44
$C_8H_{17}O_2$	9.00	0.76
$C_8H_{19}NO$	9.37	0.59
$C_8H_{21}N_2$	9.88	0.84
$C_9H_5O_2$	10.26	0.67
C_9H_7NO	10.63	0.51
$C_9H_{15}N_2$	10.99	0.75
$C_{10}H_{11}O$	11.36	0.59
$C_{11}H_{13}$	12.10	0.67
$C_{12}H$	12.98	0.77
146		
$C_4H_6N_2O_4$	5.34	0.92
$C_4H_8N_2O_3$	5.71	0.74
$C_4H_{10}N_4O_2$	6.09	0.56
$C_5H_8NO_4$	6.07	0.96
$C_5H_{10}N_2O_3$	6.44	0.78
$C_5H_{12}N_2O_2$	6.82	0.60
$C_5H_{14}N_4O$	7.19	0.43
$C_6H_2N_4O$	8.08	0.49
$C_6H_{10}O_4$	6.80	1.00
$C_6H_{12}NO_3$	7.17	0.82
$C_6H_{14}N_2O_2$	7.55	0.65
$C_6H_{16}N_2O$	7.92	0.48
$C_6H_{18}N_4$	8.30	0.31
$C_7H_2N_2O_2$	8.44	0.71
$C_7H_4N_2O$	8.81	0.55
$C_7H_6N_4$	9.19	0.38
$C_7H_{14}O_3$	7.91	0.87
$C_7H_{16}NO_2$	8.28	0.70
$C_7H_{18}N_2O$	8.65	0.53
$C_8H_2O_3$	8.79	0.94
$C_8H_4NO_2$	9.17	0.77
$C_8H_6N_2O$	9.54	0.61
$C_8H_8N_3$	9.92	0.44
$C_8H_{16}O_2$	9.01	0.76
$C_9H_6O_2$	9.90	0.84

	P + 1	P + 2
C_5H_9NO	10.27	0.68
$C_6H_{10}N_2$	10.65	0.51
$C_{12}H_{18}O$	11.01	0.75
$C_{13}H_{12}N$	11.38	0.59
$C_{11}H_{14}$	12.11	0.67
$C_{12}H_2$	13.00	0.77
147		
$C_4H_7N_2O_4$	5.35	0.92
$C_4H_9N_3O_3$	5.73	0.74
$C_4H_{11}N_4O_2$	6.10	0.56
$C_5H_9NO_4$	6.09	0.96
$C_5H_{11}N_2O_3$	6.46	0.78
$C_5H_{13}N_3O_2$	6.83	0.60
$C_6H_{13}N_4O$	7.21	0.43
$C_6HN_3O_2$	7.72	0.66
$C_6H_9N_2O$	8.10	0.49
$C_6H_{11}O_4$	6.82	1.00
$C_6H_{13}NO_3$	7.19	0.82
$C_6H_{15}N_2O_2$	7.57	0.65
$C_6H_{17}N_3O$	7.94	0.48
C_7HNO_3	8.08	0.89
$C_7H_3N_2O_2$	8.45	0.72
$C_7H_5N_3O$	8.83	0.55
$C_7H_7N_4$	9.20	0.38
$C_7H_{11}O_3$	7.92	0.87
$C_7H_{13}NO_2$	8.30	0.70
$C_8H_9O_3$	8.81	0.94
$C_8H_5NO_2$	9.19	0.78
$C_8H_7N_2O$	9.56	0.61
$C_8H_9N_2$	9.93	0.44
$C_8H_{17}O_2$	9.92	0.84
C_8H_9NO	10.29	0.68
$C_8H_{11}N_2$	10.66	0.51
$C_{10}H_{14}O$	11.02	0.75
$C_{10}H_{12}N$	11.40	0.59
$C_{11}HN$	12.28	0.69
$C_{11}H_{15}$	12.13	0.67
$C_{12}H_3$	13.02	0.78
148		
$C_4H_8N_2O_4$	5.37	0.92
$C_4H_{10}N_3O_3$	5.74	0.74
$C_4H_{12}N_4O_2$	6.12	0.56
$C_5H_{10}NO_4$	6.10	0.96
$C_5H_{12}N_2O_3$	6.48	0.78
$C_5H_{14}N_3O_2$	6.85	0.60
$C_5H_{16}N_4O$	7.22	0.43
$C_6H_2N_2O_2$	7.74	0.66
$C_6H_4N_4O$	8.11	0.49
$C_6H_{12}O_4$	6.83	1.00
$C_6H_{14}NO_3$	7.21	0.83
$C_6H_{16}N_2O_2$	7.58	0.65
$C_7H_2NO_3$	8.10	0.89
$C_7H_4N_2O_2$	8.47	0.72
$C_7H_6N_2O$	8.84	0.55
$C_7H_8N_4$	9.22	0.38
$C_7H_{16}O_3$	7.94	0.88
$C_8H_4O_3$	8.83	0.94
$C_8H_6NO_2$	9.20	0.78
$C_8H_8N_2O$	9.58	0.61
$C_8H_{10}N_3$	9.95	0.45
$C_8H_8O_2$	9.93	0.84
$C_8H_{10}NO$	10.31	0.68

	P + 1	P + 2
$C_8H_{12}N_2$	10.68	0.52
$C_9H_{12}O$	11.04	0.75
$C_9H_{14}N$	11.41	0.59
$C_{10}H_2O$	12.30	0.69
$C_{10}H_{16}$	12.14	0.67
$C_{11}H_4N$	13.03	0.78
149		
$C_4H_9N_2O_4$	5.39	0.92
$C_4H_{11}N_3O_3$	5.76	0.74
$C_4H_{13}N_4O_2$	6.13	0.56
$C_5HN_2O_2$	7.02	0.62
$C_5H_{11}NO_4$	6.12	0.96
$C_5H_{13}N_2O_3$	6.49	0.78
$C_5H_{15}N_3O_2$	6.87	0.61
C_6HNO_4	7.38	0.84
$C_6H_3N_2O_3$	7.75	0.66
$C_6H_5N_4O$	8.13	0.49
$C_6H_9O_4$	6.85	1.00
$C_6H_{15}NO_3$	7.22	0.83
C_7HO_3	7.74	1.06
$C_7H_3NO_3$	8.11	0.89
$C_7H_5N_2O_2$	8.49	0.72
$C_7H_7N_2O$	8.86	0.55
$C_7H_9N_4$	9.23	0.38
$C_8H_5O_3$	8.84	0.95
$C_8H_7NO_2$	9.22	0.78
$C_8H_9N_2O$	9.59	0.61
$C_8H_{11}N_3$	9.97	0.45
$C_8H_9O_2$	9.95	0.84
$C_8H_{11}NO$	10.32	0.68
$C_8H_{13}N_2$	10.70	0.52
C_9HNO	11.59	0.61
$C_9H_{13}O$	11.05	0.75
$C_9H_{15}N$	11.43	0.59
$C_{11}HO$	11.94	0.85
$C_{11}H_3N$	12.32	0.69
$C_{11}H_{17}$	12.16	0.67
$C_{12}H_5$	13.05	0.78
150		
$C_4H_{10}N_2O_4$	5.40	0.92
$C_4H_{12}N_3O_3$	5.78	0.74
$C_4H_{14}N_4O_2$	6.15	0.56
$C_5H_2N_4O_2$	7.04	0.62
$C_5H_{12}NO_4$	6.13	0.96
$C_5H_{14}N_2O_3$	6.51	0.78
$C_5H_{16}N_3O_2$	6.89	0.61
$C_6H_2N_2O_3$	7.40	0.84
$C_6H_4N_3O_2$	7.77	0.67
$C_6H_6N_4O$	8.15	0.49
$C_6H_{14}O_4$	6.86	1.00
$C_7H_2O_4$	7.75	1.06
$C_7H_4NO_3$	8.13	0.89
$C_7H_6N_2O_2$	8.50	0.72
$C_7H_8N_3O$	8.88	0.55
$C_7H_{10}N_4$	9.25	0.38
$C_8H_6O_3$	8.86	0.95
$C_8H_8NO_2$	9.23	0.78
$C_8H_{10}N_2O$	9.61	0.61
$C_8H_{12}N_3$	9.98	0.45
$C_8H_{10}O_2$	9.96	0.84
$C_8H_{12}NO$	10.34	0.68
$C_8H_{14}N_2$	10.71	0.52

	P + 1	P + 2
$C_{10}H_2N_2$	11.60	0.61
$C_{10}H_4O$	11.07	0.75
$C_{10}H_6N$	11.44	0.60
$C_{11}H_2O$	11.96	0.85
$C_{11}H_4N$	12.33	0.70
$C_{11}H_{18}$	12.18	0.68
$C_{12}H_6$	13.06	0.78
151		
$C_4H_{11}N_2O_4$	5.42	0.92
$C_4H_{13}N_3O_3$	5.79	0.74
$C_5HN_3O_2$	6.68	0.79
$C_5H_3N_4O_2$	7.06	0.62
$C_5H_{15}NO_4$	6.15	0.96
C_6HNO_4	7.04	1.01
$C_6H_3N_2O_3$	7.41	0.84
$C_6H_5N_4O_2$	7.79	0.67
$C_6H_7N_4O$	8.16	0.50
$C_7H_7O_4$	7.77	1.06
$C_7H_9NO_3$	8.14	0.89
$C_7H_{11}N_2O_2$	8.52	0.72
$C_7H_{13}N_3O$	8.89	0.55
$C_7H_{15}N_4$	9.27	0.39
$C_8H_7O_3$	8.87	0.95
$C_8H_9NO_2$	9.25	0.78
$C_8H_{11}N_2O$	9.62	0.62
$C_8H_{13}N_3$	10.00	0.45
C_8HN_3O	10.89	0.54
$C_8H_{11}O_2$	9.98	0.85
$C_8H_{13}NO$	10.36	0.68
$C_8H_{15}N_2$	10.73	0.52
$C_{10}HNO$	11.24	0.77
$C_{10}H_3N_2$	11.62	0.61
$C_{10}H_{15}O$	11.09	0.76
$C_{10}H_{17}N$	11.46	0.60
$C_{11}H_3O$	11.97	0.85
$C_{11}H_5N$	12.35	0.70
$C_{11}H_{19}$	12.19	0.68
$C_{12}H_7$	13.08	0.79
152		
$C_4H_{12}N_2O_4$	5.43	0.92
$C_5H_2N_2O_3$	6.70	0.79
$C_5H_4N_4O_2$	7.07	0.62
$C_6H_2NO_4$	7.05	1.01
$C_6H_4N_2O_3$	7.43	0.84
$C_6H_6N_2O_2$	7.80	0.67
$C_6H_8N_4O$	8.18	0.50
$C_7H_4O_4$	7.79	1.06
$C_7H_6NO_3$	8.16	0.89
$C_7H_8N_2O_2$	8.53	0.72
$C_7H_{10}N_3O$	8.91	0.55
$C_7H_{12}N_4$	9.28	0.39
$C_8H_8O_3$	8.89	0.95
$C_8H_{10}NO_2$	9.27	0.78
$C_8H_{12}N_2O$	9.64	0.62
$C_8H_{14}N_3$	10.01	0.45
$C_8H_2N_3$	10.90	0.54
$C_8H_{12}O_2$	10.00	0.85
$C_8H_{14}NO$	10.37	0.68
$C_8H_{16}N_2$	10.74	0.52
$C_{10}H_2NO$	11.26	0.78
$C_{10}H_4N_2$	11.63	0.62
$C_{10}H_{16}O$	11.10	0.76

	P + 1	P + 2
$C_{10}H_{18}N$	11.48	0.60
$C_{11}H_4O$	11.99	0.86
$C_{11}H_6N$	12.36	0.70
$C_{11}H_{20}$	12.21	0.68
$C_{12}H_8$	13.10	0.79
153		
$C_5HN_2O_4$	6.34	0.97
$C_5H_3N_3O_3$	6.71	0.80
$C_5H_5N_4O_2$	7.09	0.62
$C_6H_3NO_4$	7.07	1.02
$C_6H_5N_2O_3$	7.44	0.84
$C_6H_7N_2O_2$	7.82	0.67
$C_6H_9N_4O$	8.19	0.50
$C_7H_5O_4$	7.80	1.07
$C_7H_7NO_3$	8.18	0.89
$C_7H_9N_2O_2$	8.55	0.72
$C_7H_{11}N_3O$	8.92	0.56
$C_7H_{13}N_4$	9.30	0.39
C_8HN_4	10.19	0.47
$C_8H_5O_3$	8.91	0.95
$C_8H_{11}NO_2$	9.28	0.78
$C_8H_{13}N_2O$	9.66	0.62
$C_8H_{15}N_3$	10.03	0.45
C_8HN_2O	10.54	0.70
$C_8H_2N_3$	10.92	0.54
$C_8H_{13}O_2$	10.01	0.85
$C_8H_{15}NO$	10.39	0.69
$C_8H_{17}N_2$	10.76	0.52
$C_{10}HO_2$	10.90	0.94
$C_{10}H_3NO$	11.28	0.78
$C_{10}H_5N_2$	11.65	0.62
$C_{10}H_{17}O$	11.12	0.76
$C_{10}H_{19}N$	11.49	0.60
$C_{11}H_5O$	12.01	0.86
$C_{11}H_7N$	12.38	0.70
$C_{11}H_{21}$	12.22	0.68
$C_{12}H_9$	13.11	0.79
154		
$C_4H_2N_2O_4$	6.35	0.97
$C_5H_4N_3O_3$	6.73	0.80
$C_6H_6N_4O_2$	7.10	0.62
$C_6H_8NO_3$	7.09	1.02
$C_6H_{10}N_2O_2$	7.46	0.84
$C_6H_{12}N_3O_2$	7.83	0.67
$C_6H_{10}N_4O$	8.21	0.50
$C_7H_6O_4$	7.82	1.07
$C_7H_8NO_3$	8.19	0.90
$C_7H_{10}N_2O_2$	8.57	0.73
$C_7H_{12}N_3O$	8.94	0.56
$C_7H_{14}N_4$	9.31	0.39
$C_8H_2N_4$	10.20	0.47
$C_8H_6O_3$	8.92	0.95
$C_8H_{12}NO_2$	9.30	0.79
$C_8H_{14}N_2O$	9.67	0.62
$C_8H_{16}N_3$	10.05	0.46
$C_8H_2N_2O$	10.56	0.70
$C_8H_4N_3$	10.93	0.54
$C_8H_{14}O_2$	10.03	0.85
$C_8H_{16}NO$	10.40	0.69
$C_8H_{18}N_2$	10.78	0.53
$C_{10}H_4O_2$	10.92	0.94
$C_{10}H_6NO$	11.29	0.78

	P + 1	P + 2
$C_{10}H_6N_2$	11.67	0.62
$C_{10}H_{18}O$	11.13	0.76
$C_{10}H_{20}N$	11.51	0.60
$C_{11}H_6O$	12.02	0.86
$C_{11}H_8N$	12.40	0.70
$C_{11}H_{22}$	12.24	0.68
$C_{12}H_{10}$	13.13	0.79
155		
$C_5H_5N_2O_4$	6.37	0.97
$C_5H_6N_3O_3$	6.75	0.80
$C_5H_7N_4O_2$	7.12	0.62
$C_6H_5NO_4$	7.10	1.02
$C_6H_7N_2O_3$	7.48	0.84
$C_6H_9N_2O_2$	7.85	0.67
$C_6H_{11}N_4O$	8.23	0.50
$C_7H_7O_4$	7.83	1.07
$C_7H_9NO_3$	8.21	0.90
$C_7H_{11}N_2O_2$	8.58	0.73
$C_7H_{13}N_4O$	8.96	0.56
$C_7H_{15}N_4$	9.33	0.39
C_8HN_3O	9.84	0.64
$C_8H_3N_4$	10.22	0.47
$C_8H_{11}O_3$	8.94	0.95
$C_8H_{13}NO_2$	9.31	0.79
$C_8H_{15}N_2O$	9.69	0.62
$C_8H_{17}N_3$	10.06	0.46
C_9HNO_2	10.20	0.87
$C_9H_3N_2O$	10.58	0.71
$C_9H_5N_3$	10.95	0.54
$C_9H_{15}O_2$	10.04	0.85
$C_9H_{17}NO$	10.42	0.69
$C_9H_{19}N_3$	10.79	0.53
$C_{10}H_9O_2$	10.93	0.94
$C_{10}H_{11}NO$	11.31	0.78
$C_{10}H_{13}N_3$	11.68	0.62
$C_{10}H_{15}O$	11.15	0.76
$C_{10}H_{21}N$	11.52	0.60
$C_{11}H_7O$	12.04	0.86
$C_{11}H_9N$	12.41	0.71
$C_{11}H_{23}$	12.26	0.69
$C_{12}H_{11}$	13.14	0.79
156		
$C_5H_4N_2O_4$	6.39	0.98
$C_5H_6N_3O_3$	6.76	0.80
$C_5H_8N_4O_2$	7.14	0.62
$C_6H_6NO_4$	7.12	1.02
$C_6H_8N_2O_3$	7.49	0.85
$C_6H_{10}N_3O_2$	7.87	0.67
$C_6H_{12}N_4O$	8.24	0.50
$C_7H_8O_4$	7.85	1.07
$C_7H_{10}NO_3$	8.22	0.90
$C_7H_{12}N_2O_2$	8.60	0.73
$C_7H_{14}N_3O$	8.97	0.56
$C_7H_{16}N_4$	9.35	0.39
$C_8H_2N_3O$	9.86	0.64
$C_8H_4N_4$	10.24	0.47
$C_8H_{12}O_3$	8.95	0.96
$C_8H_{14}NO_2$	9.33	0.79
$C_8H_{16}N_2O$	9.70	0.62
$C_8H_{18}N_3$	10.08	0.46
$C_9H_2NO_2$	10.22	0.87
$C_9H_4N_2O$	10.59	0.71
$C_9H_6N_3$	10.97	0.55
$C_9H_{10}O_2$	10.06	0.85
$C_9H_{12}NO$	10.43	0.69
$C_9H_{14}N_3$	10.81	0.53
$C_{10}H_8O_2$	10.95	0.94
$C_{10}H_{10}NO$	11.32	0.78
$C_{10}H_{12}N_3$	11.70	0.62
$C_{10}H_{22}O$	11.17	0.77
$C_{10}H_{22}N$	11.54	0.61
$C_{11}H_8O$	12.05	0.86
$C_{11}H_{10}N$	12.43	0.71
$C_{11}H_{24}$	12.27	0.69
$C_{12}H_{12}$	13.16	0.80
157		
$C_5H_5N_2O_4$	6.40	0.98
$C_5H_7N_3O_3$	6.78	0.80
$C_5H_9N_4O_2$	7.15	0.62
$C_6H_7NO_4$	7.13	1.02
$C_6H_9N_2O_3$	7.51	0.85
$C_6H_{11}N_3O_2$	7.88	0.67
$C_6H_{13}N_4O$	8.26	0.50
C_7HNO_4	9.15	0.57
$C_7H_9O_4$	7.87	1.07
$C_7H_{11}NO_3$	8.24	0.90
$C_7H_{13}N_2O_2$	8.61	0.73
$C_7H_{15}N_3O$	8.99	0.56
$C_7H_{17}N_4$	9.36	0.39
$C_8HN_2O_2$	9.50	0.80
$C_8H_3N_3O$	9.88	0.64
$C_8H_5N_4$	10.25	0.48
$C_8H_{13}O_3$	8.97	0.96
$C_8H_{15}NO_2$	9.35	0.79
$C_8H_{17}N_2O$	9.72	0.62
$C_8H_{19}N_3$	10.09	0.46
C_9HO_3	9.86	1.03
$C_9H_3NO_2$	10.23	0.87
$C_9H_5N_2O$	10.61	0.71
$C_9H_7N_3$	10.98	0.55
$C_9H_{17}O_2$	10.08	0.86
$C_9H_{19}NO$	10.45	0.69
$C_9H_{21}N_2$	10.82	0.53
$C_{10}H_5O_2$	10.96	0.94
$C_{10}H_7NO$	11.34	0.78
$C_{10}H_9N_2$	11.71	0.63
$C_{10}H_{21}O$	11.18	0.77
$C_{10}H_{23}N$	11.56	0.61
$C_{11}H_9O$	12.07	0.86
$C_{11}H_{11}N$	12.44	0.72
$C_{12}H_{13}$	13.18	0.80
$C_{13}H$	14.06	0.91
158		
$C_5H_6N_2O_4$	6.42	0.98
$C_5H_8N_3O_3$	6.79	0.80
$C_5H_{10}N_4O_2$	7.17	0.63
$C_6H_8NO_4$	7.15	1.02
$C_6H_{10}N_2O_3$	7.52	0.85
$C_6H_{12}N_3O_2$	7.90	0.68
$C_6H_{14}N_4O$	8.27	0.50
$C_7H_2N_2O$	9.16	0.58
$C_7H_{10}O_4$	7.88	1.07
$C_7H_{12}NO_3$	8.26	0.90
$C_7H_{14}N_2O_2$	8.63	0.73
$C_7H_{16}N_3O$	9.00	0.56
$C_7H_{18}N_4$	9.38	0.40
$C_8H_2N_2O_2$	9.52	0.81
$C_8H_4N_3O$	9.89	0.64
$C_8H_6N_4$	10.27	0.48
$C_8H_{14}O_3$	8.99	0.96
$C_8H_{16}NO_2$	9.36	0.79
$C_8H_{18}N_2O$	9.74	0.63
$C_8H_{20}N_3$	10.11	0.46
$C_9H_8O_3$	9.88	1.04
$C_9H_{10}NO_2$	10.25	0.87
$C_9H_{12}N_2O$	10.62	0.71
$C_9H_{14}N_3$	11.00	0.55
$C_{10}H_{10}O_2$	10.09	0.86
$C_{10}H_{12}NO$	10.47	0.69
$C_{10}H_{14}N_2$	10.84	0.53
$C_{10}H_{24}O$	10.98	0.95
$C_{10}H_{24}NO$	11.36	0.79
$C_{10}H_{26}N_2$	11.73	0.63
$C_{11}H_{12}O$	11.20	0.77
$C_{11}H_{14}N$	12.09	0.87
$C_{11}H_{26}N$	12.46	0.71
$C_{12}H_{14}$	13.19	0.80
$C_{13}H_2$	14.08	0.92
159		
$C_5H_7N_2O_4$	6.43	0.98
$C_5H_9N_3O_3$	6.81	0.80
$C_5H_{11}N_4O_2$	7.18	0.63
$C_6H_9NO_4$	7.17	1.02
$C_6H_{11}N_2O_3$	7.54	0.85
$C_6H_{13}N_3O_2$	7.91	0.68
$C_6H_{15}N_4O$	8.29	0.51
C_7HNO_4	8.80	0.75
$C_7H_3N_4O$	9.18	0.58
$C_7H_{11}O_4$	7.90	1.07
$C_7H_{13}NO_3$	8.27	0.90
$C_7H_{15}N_2O_2$	8.65	0.73
$C_7H_{17}N_3O$	9.02	0.56
$C_7H_{19}N_4$	9.39	0.40
C_8HNO_3	9.16	0.97
$C_8H_3N_2O_2$	9.53	0.81
$C_8H_5N_3O$	9.91	0.64
$C_8H_7N_4$	10.28	0.48
$C_8H_{15}O_3$	9.00	0.96
$C_8H_{17}NO_2$	9.38	0.79
$C_8H_{19}N_2O$	9.75	0.63
$C_8H_{21}N_3$	10.13	0.46
$C_9H_9O_3$	9.89	1.04
$C_9H_{11}NO_2$	10.27	0.87
$C_9H_{13}N_2O$	10.64	0.71
$C_9H_{15}N_3$	11.01	0.55
$C_{10}H_{11}O_2$	10.11	0.86
$C_{10}H_{13}NO$	10.48	0.70
$C_{10}H_7O_2$	11.00	0.95
$C_{10}H_9NO$	11.37	0.79
$C_{10}H_{11}N_2$	11.75	0.63
$C_{11}H_{11}O$	12.10	0.87
$C_{11}H_{13}N$	12.48	0.71
$C_{12}HN$	13.37	0.82
$C_{12}H_{15}$	13.21	0.80
$C_{13}H_3$	14.10	0.92
160		
$C_5H_8N_2O_4$	6.45	0.98
$C_5H_{10}N_3O_3$	6.83	0.80
$C_5H_{12}N_4O_2$	7.20	0.63
$C_6H_{10}NO_4$	7.18	1.02
$C_6H_{12}N_2O_3$	7.56	0.85
$C_6H_{14}N_3O_2$	7.93	0.68
$C_6H_{16}N_4O$	8.31	0.51
$C_7H_2N_2O_2$	8.82	0.75
$C_7H_4N_3O$	9.19	0.58
$C_7H_6O_4$	7.91	1.07
$C_7H_{14}NO_3$	8.29	0.90
$C_7H_{16}N_2O_2$	8.66	0.73
$C_7H_{18}N_3O$	9.04	0.57
$C_7H_{20}N_4$	9.41	0.40
$C_8H_2NO_3$	9.18	0.97
$C_8H_4N_2O_2$	9.55	0.81
$C_8H_6N_3O$	9.92	0.64
$C_8H_8N_4$	10.30	0.48
$C_8H_{16}O_3$	9.02	0.96
$C_8H_{18}NO_2$	9.39	0.79
$C_8H_{20}N_2O$	9.77	0.63
$C_8H_4O_3$	9.91	1.04
$C_8H_6NO_3$	10.28	0.88
$C_8H_8N_2O$	10.66	0.71
$C_8H_{10}N_3$	11.03	0.55
$C_8H_{20}O_2$	10.12	0.86
$C_{10}H_{12}O_2$	11.01	0.95
$C_{10}H_{14}NO$	11.39	0.79
$C_{10}H_{16}N_2$	11.76	0.63
$C_{11}H_{12}O$	12.12	0.87
$C_{11}H_{14}N$	12.49	0.72
$C_{12}H_2N$	13.38	0.82
$C_{12}H_{16}$	13.22	0.80
$C_{13}H_4$	14.11	0.92
161		
$C_5H_9N_2O_4$	6.47	0.98
$C_5H_{11}N_3O_3$	6.84	0.80
$C_5H_{13}N_4O_2$	7.22	0.63
$C_6H_{11}NO_4$	7.20	1.03
$C_6H_{13}N_2O_3$	7.57	0.85
$C_6H_{15}N_3O_2$	7.95	0.68
$C_6H_{17}N_4O$	8.32	0.51
$C_7HN_2O_3$	8.46	0.92
$C_7H_3N_3O_2$	8.84	0.75
$C_7H_5N_4O$	9.21	0.58
$C_7H_{13}O_4$	7.93	1.08
$C_7H_{15}NO_3$	8.30	0.90
$C_7H_{17}N_2O_2$	8.68	0.74
$C_7H_{19}N_3O$	9.05	0.57
C_8HO_4	8.82	1.14
$C_8H_3NO_3$	9.19	0.98
$C_8H_5N_2O_2$	9.57	0.81
$C_8H_7N_3O$	9.94	0.65
$C_8H_9N_4$	10.32	0.48
$C_8H_{17}O_3$	9.03	0.96
$C_8H_{19}NO_2$	9.41	0.80
$C_9H_5O_3$	9.92	1.04
$C_9H_7NO_2$	10.30	0.88
$C_9H_9N_2O$	10.67	0.72
$C_9H_{11}N_3$	11.05	0.56

	P + 1	P + 2
$C_{10}H_8O_2$	11.03	0.95
$C_{10}H_{11}NO$	11.40	0.79
$C_{10}H_{12}N_2$	11.78	0.63
$C_{11}HN_2$	12.67	0.74
$C_{11}H_{13}O$	12.13	0.87
$C_{11}H_{13}N$	12.51	0.72
$C_{12}HO$	13.02	0.98
$C_{12}H_3N$	13.40	0.83
$C_{12}H_{17}$	13.24	0.81
$C_{13}H_5$	14.13	0.92
162		
$C_5H_{10}N_2O_4$	6.48	0.98
$C_5H_{12}N_2O_3$	6.86	0.81
$C_5H_{14}N_4O_2$	7.23	0.63
$C_6H_2N_4O_2$	8.12	0.69
$C_6H_{12}NO_4$	7.21	1.03
$C_6H_{14}N_2O_3$	7.59	0.85
$C_6H_{16}N_3O_2$	7.96	0.68
$C_6H_{18}N_4O$	8.34	0.51
$C_7H_2N_2O_3$	8.48	0.92
$C_7H_4N_3O_2$	8.85	0.75
$C_7H_6N_4O$	9.23	0.58
$C_7H_{14}O_4$	7.95	1.08
$C_7H_{16}NO_3$	8.32	0.91
$C_7H_{18}N_2O_2$	8.69	0.74
$C_8H_2O_4$	8.83	1.15
$C_8H_4NO_3$	9.21	0.98
$C_8H_6N_2O_2$	9.58	0.81
$C_8H_8N_3O$	9.96	0.65
$C_8H_{10}N_4$	10.33	0.48
$C_8H_{16}O_3$	9.05	0.96
$C_8H_6O_3$	9.94	1.04
$C_8H_8NO_2$	10.31	0.88
$C_8H_{10}N_2O$	10.69	0.72
$C_8H_{12}N_3$	11.06	0.56
$C_{10}H_{10}O_2$	11.04	0.95
$C_{10}H_{13}NO$	11.42	0.79
$C_{10}H_{14}N_2$	11.79	0.64
$C_{11}H_2N_2$	12.68	0.74
$C_{11}H_{14}O$	12.15	0.87
$C_{11}H_{16}N$	12.52	0.72
$C_{12}H_2O$	13.04	0.98
$C_{12}H_4N$	13.41	0.83
$C_{12}H_{18}$	13.26	0.81
$C_{13}H_6$	14.14	0.92
163		
$C_5H_{11}N_2O_4$	6.50	0.98
$C_5H_{13}N_3O_3$	6.87	0.81
$C_5H_{15}N_4O_2$	7.25	0.63
$C_6HN_3O_3$	7.76	0.87
$C_6H_3N_4O_2$	8.14	0.69
$C_6H_{13}NO_4$	7.23	1.03
$C_6H_{15}N_2O_3$	7.60	0.85
$C_6H_{17}N_3O_2$	7.98	0.68
C_7HNO_4	8.12	1.09
$C_7H_3N_2O_3$	8.49	0.92
$C_7H_5N_3O_2$	8.87	0.75
$C_7H_7N_4O$	9.24	0.58
$C_7H_{15}O_3$	7.96	1.08
$C_7H_{17}NO_3$	8.34	0.91
$C_8H_9O_4$	8.85	1.15
$C_8H_9NO_3$	9.22	0.98
$C_8H_7N_2O_2$	9.60	0.81
$C_8H_9N_3O$	9.97	0.65
$C_8H_{11}N_4$	10.35	0.49
$C_8H_7O_3$	9.96	1.04
$C_8H_9NO_2$	10.33	0.88
$C_8H_{11}N_2O$	10.70	0.72
$C_8H_{13}N_3$	11.08	0.56
$C_{10}HN_3$	11.97	0.66
$C_{10}H_{11}O_2$	11.06	0.95
$C_{10}H_{13}NO$	11.44	0.80
$C_{10}H_{15}N_2$	11.81	0.64
$C_{11}HNO$	12.32	0.89
$C_{11}H_3N_2$	12.70	0.74
$C_{11}H_{15}O$	12.17	0.88
$C_{11}H_{17}N$	12.54	0.72
$C_{12}H_3O$	13.05	0.98
$C_{12}H_5N$	13.43	0.83
$C_{12}H_{19}$	13.27	0.81
$C_{13}H_7$	14.16	0.93
164		
$C_5H_{12}N_2O_4$	6.51	0.98
$C_5H_{14}N_3O_3$	6.89	0.81
$C_5H_{16}N_4O_2$	7.26	0.63
$C_6H_2N_3O_3$	7.78	0.87
$C_6H_4N_4O_2$	8.15	0.70
$C_6H_{14}NO_4$	7.25	1.03
$C_6H_{16}N_2O_3$	7.62	0.86
$C_7H_2NO_4$	8.13	1.09
$C_7H_4N_2O_3$	8.51	0.92
$C_7H_6N_3O_2$	8.88	0.75
$C_7H_8N_4O$	9.26	0.59
$C_7H_{16}O_4$	7.98	1.08
$C_8H_4O_4$	8.87	1.15
$C_8H_6NO_3$	9.24	0.98
$C_8H_8N_2O_2$	9.61	0.81
$C_8H_{10}N_3O$	9.99	0.65
$C_8H_{12}N_4$	10.36	0.49
$C_8H_8O_3$	9.97	1.05
$C_8H_{10}NO_2$	10.35	0.88
$C_8H_{12}N_2O$	10.72	0.72
$C_8H_{14}N_3$	11.09	0.56
$C_{10}H_2N_3$	11.98	0.66
$C_{10}H_{12}O_2$	11.08	0.96
$C_{10}H_{14}NO$	11.45	0.80
$C_{10}H_{16}N_2$	11.83	0.64
$C_{11}H_2NO$	12.34	0.90
$C_{11}H_4N_2$	12.71	0.74
$C_{11}H_{16}O$	12.18	0.88
$C_{11}H_{18}N$	12.56	0.72
$C_{12}H_4O$	13.07	0.98
$C_{12}H_6N$	13.45	0.83
$C_{12}H_{20}$	13.29	0.81
$C_{13}H_8$	14.18	0.93
165		
$C_5H_{13}N_2O_4$	6.53	0.98
$C_5H_{15}N_3O_3$	6.91	0.81
$C_6HN_2O_4$	7.42	1.04
$C_6H_3N_3O_3$	7.79	0.87
$C_6H_5N_4O_2$	8.17	0.70
$C_6H_{15}NO_4$	7.26	1.03
$C_7H_3NO_4$	8.15	1.09
$C_7H_5N_2O_3$	8.52	0.92
$C_7H_7N_3O_2$	8.90	0.75
$C_7H_9N_4O$	9.27	0.59
$C_7H_5O_4$	8.88	1.15
$C_7H_7NO_3$	9.26	0.98
$C_7H_9N_2O_2$	9.63	0.82
$C_7H_{11}N_3O$	10.00	0.65
$C_7H_{13}N_4$	10.38	0.49
C_7HN_4	11.27	0.58
$C_7H_9O_3$	9.99	1.05
$C_7H_{11}NO_2$	10.36	0.88
$C_7H_{13}N_2O$	10.74	0.72
$C_7H_{15}N_3$	11.11	0.56
C_9HN_2O	11.62	0.82
$C_9H_3N_3$	12.00	0.66
$C_9H_{13}O_2$	11.09	0.96
$C_9H_{15}NO$	11.47	0.80
$C_9H_{17}N_2$	11.84	0.64
$C_{11}HO_2$	11.98	1.05
$C_{11}H_3NO$	12.36	0.90
$C_{11}H_5N_2$	12.73	0.74
$C_{11}H_{17}O$	12.20	0.88
$C_{11}H_{19}N$	12.57	0.73
$C_{12}H_5O$	13.09	0.99
$C_{12}H_7N$	13.46	0.84
$C_{12}H_{21}$	13.30	0.81
$C_{13}H_9$	14.19	0.93
166		
$C_5H_{14}N_2O_4$	6.55	0.99
$C_6H_2N_2O_4$	7.44	1.04
$C_6H_4N_3O_3$	7.81	0.87
$C_6H_6N_4O_2$	8.18	0.70
$C_7H_4NO_4$	8.17	1.09
$C_7H_6N_2O_3$	8.54	0.92
$C_7H_8N_3O_2$	8.92	0.76
$C_7H_{10}N_4O$	9.29	0.59
$C_8H_6O_4$	8.90	1.15
$C_8H_8NO_3$	9.27	0.98
$C_8H_{10}N_2O_2$	9.65	0.82
$C_8H_{12}N_3O$	10.02	0.65
$C_8H_{14}N_4$	10.40	0.49
$C_8H_2N_4$	11.28	0.58
$C_8H_{10}O_3$	10.00	1.05
$C_8H_{12}NO_2$	10.38	0.89
$C_8H_{14}N_2O$	10.75	0.72
$C_8H_{16}N_3$	11.13	0.56
$C_{10}H_2N_2O$	11.64	0.82
$C_{10}H_4N_3$	12.01	0.66
$C_{10}H_{14}O_2$	11.11	0.96
$C_{10}H_{16}NO$	11.48	0.80
$C_{10}H_{18}N_2$	11.86	0.64
$C_{11}H_2O_2$	12.00	1.06
$C_{11}H_4NO$	12.37	0.90
$C_{11}H_6N_2$	12.75	0.75
$C_{11}H_{18}O$	12.21	0.88
$C_{11}H_{20}N$	12.59	0.73
$C_{12}H_6O$	13.10	0.99
$C_{12}H_8N$	13.48	0.84
$C_{12}H_{22}$	13.32	0.82
$C_{13}H_{10}$	14.21	0.93
167		
$C_6H_3N_2O_4$	7.45	1.04
$C_6H_5N_3O_3$	7.83	0.87
$C_6H_7N_4O_2$	8.20	0.70
$C_7H_5NO_4$	8.18	1.10
$C_7H_7N_2O_3$	8.56	0.93
$C_7H_9N_3O_2$	8.93	0.76
$C_7H_{11}N_4O$	9.31	0.59
$C_8H_7O_4$	8.91	1.15
$C_8H_9NO_3$	9.29	0.99
$C_8H_{11}N_2O_2$	9.66	0.82
$C_8H_{13}N_3O$	10.04	0.66
$C_8H_{15}N_4$	10.41	0.49
C_8HN_3O	10.93	0.74
$C_8H_3N_4$	11.30	0.58
$C_8H_{11}O_3$	10.02	1.05
$C_8H_{13}NO_2$	10.39	0.89
$C_8H_{15}N_2O$	10.77	0.73
$C_8H_{17}N_3$	11.14	0.57
C_9HNO_2	11.28	0.98
$C_9H_3N_2O$	11.66	0.82
$C_9H_5N_3$	12.03	0.66
$C_9H_{15}O_2$	11.12	0.96
$C_9H_{17}NO$	11.50	0.80
$C_9H_{19}N_2$	11.87	0.65
$C_{11}H_3O_2$	12.01	1.06
$C_{11}H_5NO$	12.39	0.90
$C_{11}H_7N_2$	12.76	0.75
$C_{11}H_{19}O$	12.23	0.88
$C_{11}H_{21}N$	12.60	0.73
$C_{12}H_7O$	13.12	0.99
$C_{12}H_9N$	13.49	0.84
$C_{12}H_{23}$	13.34	0.82
$C_{13}H_{11}$	14.22	0.94
168		
$C_6H_4N_2O_4$	7.47	1.04
$C_6H_6N_3O_3$	7.84	0.87
$C_6H_8N_4O_2$	8.22	0.70
$C_7H_6NO_4$	8.20	1.10
$C_7H_8N_2O_3$	8.57	0.93
$C_7H_{10}N_3O_2$	8.95	0.76
$C_7H_{12}N_4O$	9.32	0.59
$C_8H_8O_4$	8.93	1.15
$C_8H_{10}NO_3$	9.30	0.99
$C_8H_{12}N_2O_2$	9.68	0.82
$C_8H_{14}N_3O$	10.05	0.66
$C_8H_{16}N_4$	10.43	0.49
$C_9H_2N_2O$	10.94	0.74
$C_9H_4N_3$	11.32	0.58
$C_9H_{12}O_2$	10.04	1.05
$C_9H_{14}NO_2$	10.41	0.89
$C_9H_{16}N_2O$	10.78	0.73
$C_9H_{18}N_3$	11.16	0.57
$C_{10}H_2NO_2$	11.30	0.98
$C_{10}H_4N_2O$	11.67	0.82
$C_{10}H_6N_3$	12.05	0.67
$C_{10}H_{16}O_2$	11.14	0.96
$C_{10}H_{18}NO$	11.52	0.80
$C_{10}H_{20}N_2$	11.89	0.65
$C_{11}H_4O_2$	12.03	1.06
$C_{11}H_6NO$	12.40	0.90
$C_{11}H_8N_2$	12.78	0.75
$C_{11}H_{20}O$	12.25	0.89
$C_{11}H_{22}N$	12.62	0.73

	P + 1	P + 2
$C_{12}H_8O$	13.13	0.99
$C_{12}H_{10}N$	13.51	0.84
$C_{12}H_{24}$	13.35	0.82
$C_{13}H_{12}$	14.24	0.94
169		
$C_8H_5N_2O_4$	7.48	1.05
$C_8H_7N_3O_3$	7.86	0.87
$C_8H_8N_4O_2$	8.23	0.70
$C_7H_7NO_4$	8.21	1.10
$C_7H_9N_3O_3$	8.59	0.93
$C_7H_{11}N_3O_2$	8.96	0.76
$C_7H_{13}N_4O$	9.34	0.59
C_8HN_4O	10.23	0.67
$C_8H_9O_4$	8.95	1.16
$C_8H_{11}NO_3$	9.32	0.99
$C_8H_{13}N_2O_2$	9.69	0.82
$C_8H_{15}N_3O$	10.07	0.66
$C_8H_{17}N_4$	10.44	0.50
$C_9HN_2O_3$	10.58	0.91
$C_9H_{13}NO$	10.96	0.75
$C_9H_{15}N_4$	11.33	0.59
$C_9H_{13}O_3$	10.05	1.05
$C_9H_{15}NO_2$	10.43	0.89
$C_9H_{17}N_2O$	10.80	0.73
$C_9H_{19}N_3$	11.17	0.57
$C_{10}HO_3$	10.94	1.14
$C_{10}H_9NO_2$	11.31	0.98
$C_{10}H_{11}N_2O$	11.69	0.82
$C_{10}H_{13}N_3$	12.06	0.67
$C_{10}H_{17}O_2$	11.16	0.96
$C_{10}H_{15}NO$	11.53	0.81
$C_{10}H_{21}N_2$	11.91	0.65
$C_{11}H_5O_2$	12.05	1.06
$C_{11}H_7NO$	12.42	0.91
$C_{11}H_9N_2$	12.79	0.75
$C_{11}H_{21}O$	12.26	0.89
$C_{11}H_{23}N$	12.64	0.73
$C_{12}H_9O$	13.15	1.00
$C_{12}H_{11}N$	13.53	0.84
$C_{12}H_{25}$	13.37	0.82
$C_{13}H_{13}$	14.26	0.94
$C_{14}H$	15.14	1.07
170		
$C_6H_6N_2O_4$	7.50	1.05
$C_6H_8N_3O_3$	7.87	0.87
$C_6H_{10}N_4O_2$	8.25	0.70
$C_7H_8NO_4$	8.23	1.10
$C_7H_{10}N_2O_3$	8.60	0.93
$C_7H_{12}N_3O_2$	8.98	0.76
$C_7H_{14}N_4O$	9.35	0.59
$C_8H_2N_4O$	10.24	0.68
$C_8H_{10}O_4$	8.96	1.16
$C_8H_{12}NO_3$	9.34	0.99
$C_8H_{14}N_2O_2$	9.71	0.82
$C_8H_{16}N_3O$	10.08	0.66
$C_8H_{18}N_4$	10.46	0.50
$C_9H_2N_2O_2$	10.60	0.91
$C_9H_4N_3O$	10.97	0.75
$C_9H_6N_4$	11.35	0.59
$C_9H_{14}O_3$	10.07	1.06
$C_9H_{16}NO_2$	10.44	0.89
$C_9H_{18}N_2O$	10.82	0.73
$C_9H_{20}N_3$	11.19	0.57
$C_{10}H_{12}O_3$	10.96	1.14
$C_{10}H_{14}NO_2$	11.33	0.98
$C_{10}H_6N_2O$	11.70	0.83
$C_{10}H_8N_3$	12.08	0.67
$C_{10}H_{14}O_2$	11.17	0.97
$C_{10}H_{16}NO$	11.55	0.81
$C_{10}H_{22}N_2$	11.92	0.65
$C_{11}H_6O_2$	12.06	1.06
$C_{11}H_8NO$	12.44	0.91
$C_{11}H_{10}N_2$	12.81	0.75
$C_{11}H_{22}O$	12.28	0.89
$C_{11}H_{24}N$	12.65	0.74
$C_{12}H_{10}O$	13.17	1.00
$C_{12}H_{12}N$	13.54	0.85
$C_{12}H_{26}$	13.38	0.83
$C_{13}H_{14}$	14.27	0.94
$C_{14}H_2$	15.16	1.07
171		
$C_8H_7N_2O_4$	7.52	1.05
$C_8H_9N_3O_3$	7.89	0.88
$C_8H_{11}N_4O_2$	8.26	0.70
$C_7H_9NO_4$	8.25	1.10
$C_7H_{11}N_2O_3$	8.62	0.93
$C_7H_{13}N_3O_2$	9.00	0.76
$C_7H_{15}N_4O$	9.37	0.60
$C_8H_3NO_2$	9.88	0.84
$C_8H_5N_4O$	10.26	0.68
$C_8H_{11}O_4$	8.98	1.16
$C_8H_{13}NO_3$	9.35	0.99
$C_8H_{15}N_2O_2$	9.73	0.83
$C_8H_{17}N_3O$	10.10	0.66
$C_8H_{19}N_4$	10.48	0.50
C_9HNO_3	10.24	1.07
$C_9H_3N_2O_2$	10.61	0.91
$C_9H_5N_3O$	10.99	0.75
$C_9H_7N_4$	11.36	0.59
$C_9H_{15}O_3$	10.08	1.06
$C_9H_{17}NO_2$	10.46	0.89
$C_9H_{19}N_2O$	10.83	0.73
$C_9H_{21}N_3$	11.21	0.57
$C_{10}H_5O_3$	10.97	1.14
$C_{10}H_7NO_2$	11.35	0.99
$C_{10}H_9N_2O$	11.72	0.83
$C_{10}H_{11}N_3$	12.09	0.67
$C_{10}H_{15}O_2$	11.19	0.97
$C_{10}H_{17}NO$	11.56	0.81
$C_{10}H_{23}N_2$	11.94	0.65
$C_{11}H_7O_2$	12.08	1.07
$C_{11}H_9NO$	12.45	0.91
$C_{11}H_{11}N_2$	12.83	0.76
$C_{11}H_{23}O$	12.29	0.89
$C_{11}H_{25}N$	12.67	0.74
$C_{12}H_{11}O$	13.18	1.00
$C_{12}H_{13}N$	13.56	0.85
$C_{13}HN$	14.45	0.97
$C_{13}H_{15}$	14.29	0.94
$C_{14}H_3$	15.18	1.07
172		
$C_6H_8N_2O_4$	7.53	1.05
$C_6H_{10}N_3O_3$	7.91	0.88
$C_6H_{12}N_4O_2$	8.28	0.71
$C_7H_{10}NO_4$	8.26	1.10
$C_7H_{12}N_2O_3$	8.64	0.93
$C_7H_{14}N_3O_2$	9.01	0.76
$C_7H_{16}N_4O$	9.39	0.60
$C_8H_2N_3O_2$	9.90	0.84
$C_8H_4N_4O$	10.27	0.68
$C_8H_{12}O_4$	8.99	1.16
$C_8H_{14}NO_3$	9.37	0.99
$C_8H_{16}N_2O_2$	9.74	0.83
$C_8H_{18}N_3O$	10.12	0.66
$C_8H_{20}N_4$	10.49	0.50
$C_9H_2NO_3$	10.26	1.07
$C_9H_4N_2O_2$	10.63	0.91
$C_9H_6N_3O$	11.01	0.75
$C_9H_8N_4$	11.38	0.59
$C_9H_{16}O_3$	10.10	1.06
$C_9H_{18}NO_2$	10.47	0.90
$C_9H_{20}N_2O$	10.85	0.73
$C_9H_{22}N_3$	11.22	0.57
$C_{10}H_4O_3$	10.99	1.15
$C_{10}H_6NO_2$	11.36	0.99
$C_{10}H_8N_2O$	11.74	0.83
$C_{10}H_{10}N_3$	12.11	0.67
$C_{10}H_{14}O_2$	11.20	0.97
$C_{10}H_{16}NO$	11.58	0.81
$C_{10}H_{22}N_2$	11.95	0.65
$C_{11}H_8O_2$	12.09	1.07
$C_{11}H_{10}NO$	12.47	0.91
$C_{11}H_{12}N_2$	12.84	0.76
$C_{11}H_{24}O$	12.31	0.89
$C_{12}H_{12}O$	13.20	1.00
$C_{12}H_{14}N$	13.57	0.85
$C_{13}H_2N$	14.46	0.97
$C_{13}H_{16}$	14.30	0.95
$C_{14}H_4$	15.19	1.07
173		
$C_6H_9N_2O_4$	7.55	1.05
$C_6H_{11}N_3O_3$	7.92	0.88
$C_6H_{13}N_4O_2$	8.30	0.71
$C_7HN_4O_2$	9.18	0.78
$C_7H_{11}NO_4$	8.28	1.10
$C_7H_{13}N_2O_3$	8.65	0.93
$C_7H_{15}N_3O_2$	9.03	0.77
$C_7H_{17}N_4O$	9.40	0.60
$C_8HN_2O_3$	9.54	1.01
$C_8H_3N_3O_2$	9.92	0.84
$C_8H_5N_4O$	10.29	0.68
$C_8H_{13}O_4$	9.01	1.16
$C_8H_{15}NO_3$	9.38	0.99
$C_8H_{17}N_2O_2$	9.76	0.83
$C_8H_{19}NO$	10.13	0.66
$C_8H_{21}N_4$	10.51	0.50
C_9HO_4	9.90	1.24
$C_9H_3NO_3$	10.27	1.08
$C_9H_5N_2O_2$	10.65	0.91
C_9H_7NO	11.02	0.75
$C_9H_9N_4$	11.40	0.59
$C_9H_{17}O_3$	10.12	1.06
$C_9H_{19}NO_2$	10.49	0.90
$C_9H_{21}N_2O$	10.86	0.74
$C_9H_{23}N_3$	11.24	0.58
$C_{10}H_5O_3$	11.00	1.15
$C_{10}H_7NO_2$	11.38	0.99
$C_{10}H_9N_2O$	11.75	0.83
$C_{10}H_{11}N_3$	12.13	0.67
$C_{10}H_{21}O_2$	11.22	0.97
$C_{10}H_{23}NO$	11.60	0.81
$C_{11}H_9O_2$	12.11	1.07
$C_{11}H_{11}NO$	12.48	0.91
$C_{11}H_{13}N_2$	12.86	0.76
$C_{12}HN_2$	13.75	0.87
$C_{12}H_{13}O$	13.21	1.00
$C_{12}H_{15}N$	13.59	0.85
$C_{13}HO$	14.10	1.12
$C_{13}H_3N$	14.48	0.97
$C_{13}H_{17}$	14.32	0.95
$C_{14}H_5$	15.21	1.07
174		
$C_6H_{10}N_2O_4$	7.56	1.05
$C_6H_{12}N_3O_3$	7.94	0.88
$C_6H_{14}N_4O_2$	8.31	0.71
$C_7H_2N_4O_2$	9.20	0.78
$C_7H_{12}NO_4$	8.29	1.10
$C_7H_{14}N_3O_3$	8.67	0.93
$C_7H_{16}N_4O_2$	9.04	0.77
$C_8H_4N_4O$	9.42	0.60
$C_8H_2N_2O_3$	9.56	1.01
$C_8H_4N_3O_2$	9.93	0.85
$C_8H_6N_4O$	10.31	0.68
$C_8H_{14}O_4$	9.03	1.16
$C_8H_{16}NO_3$	9.40	1.00
$C_8H_{18}N_2O_2$	9.77	0.83
$C_8H_{20}N_3O$	10.15	0.67
$C_8H_{22}N_4$	10.52	0.50
$C_9H_2O_4$	9.91	1.24
$C_9H_4NO_3$	10.29	1.08
$C_9H_6N_2O_2$	10.66	0.92
$C_9H_8N_3O$	11.04	0.75
$C_9H_{10}N_4$	11.41	0.60
$C_9H_{18}O_3$	10.13	1.06
$C_9H_{20}NO_2$	10.51	0.90
$C_9H_{22}N_2O$	10.88	0.74
$C_{10}H_6O_3$	11.02	1.15
$C_{10}H_8NO_2$	11.39	0.99
$C_{10}H_{10}N_2O$	11.77	0.83
$C_{10}H_{12}N_3$	12.14	0.68
$C_{10}H_{22}O_2$	11.24	0.97
$C_{11}H_{10}O_2$	12.13	1.07
$C_{11}H_{12}NO$	12.50	0.92
$C_{11}H_{14}N_2$	12.87	0.76
$C_{12}H_2N_2$	13.76	0.88
$C_{12}H_{14}O$	13.23	1.01
$C_{12}H_{16}N$	13.61	0.85
$C_{13}H_2O$	14.12	1.12
$C_{13}H_4N$	14.49	0.97
$C_{13}H_{18}$	14.34	0.95
$C_{14}H_6$	15.22	1.08
175		
$C_6H_{11}N_2O_4$	7.58	1.05
$C_6H_{13}N_3O_3$	7.95	0.88
$C_6H_{15}N_4O_2$	8.33	0.71
$C_7HN_3O_3$	8.84	0.95

	P + 1	P + 2
$C_7H_8N_4O_2$	9.22	0.78
$C_7H_{13}NO_4$	8.31	1.11
$C_7H_{15}N_2O_3$	8.68	0.94
$C_7H_{17}N_3O_2$	9.06	0.77
$C_7H_{19}N_4O$	9.43	0.60
C_8HNO_4	9.20	1.18
$C_8H_3N_2O_3$	9.57	1.01
$C_8H_5N_2O_2$	9.95	0.85
$C_8H_7N_4O$	10.32	0.68
$C_8H_{17}NO_3$	9.42	1.00
$C_8H_{19}N_2O_2$	9.79	0.83
$C_8H_{21}N_3O$	10.16	0.67
$C_8H_{15}O_4$	9.04	1.16
$C_8H_3O_4$	9.93	1.24
$C_8H_5NO_3$	10.30	1.08
$C_8H_7N_2O_2$	10.68	0.92
$C_8H_9N_3O$	11.05	0.76
$C_8H_{11}N_4$	11.43	0.60
$C_8H_{13}O_3$	10.15	1.06
$C_8H_{15}NO_2$	10.52	0.90
$C_{10}H_7O_3$	11.04	1.15
$C_{10}H_9NO_2$	11.41	0.99
$C_{10}H_{11}N_2O$	11.78	0.83
$C_{10}H_{13}N_3$	12.16	0.68
$C_{11}HN_3$	13.05	0.78
$C_{11}H_{11}O_2$	12.14	1.07
$C_{11}H_{13}NO$	12.52	0.92
$C_{11}H_{15}N_2$	12.89	0.77
$C_{12}HNO$	13.40	1.03
$C_{12}H_3N_2$	13.78	0.88
$C_{12}H_{15}O$	13.25	1.01
$C_{12}H_{17}N$	13.62	0.86
$C_{13}H_5O$	14.14	1.12
$C_{13}H_7N$	14.51	0.98
$C_{13}H_{18}$	14.35	0.95
$C_{14}H_7$	15.24	1.08
176		
$C_6H_{12}N_2O_4$	7.60	1.05
$C_6H_{14}N_3O_3$	7.97	0.88
$C_6H_{16}N_4O_2$	8.34	0.71
$C_7H_2N_2O_3$	8.86	0.95
$C_7H_4N_4O_2$	9.23	0.78
$C_7H_4NO_4$	8.33	1.11
$C_7H_{16}N_2O_3$	8.70	0.94
$C_7H_{18}N_3O_2$	9.08	0.77
$C_7H_{20}N_4O$	9.45	0.60
$C_8H_2NO_4$	9.22	1.18
$C_8H_4N_2O_3$	9.59	1.01
$C_8H_6N_3O_2$	9.96	0.85
$C_8H_8N_4O$	10.34	0.69
$C_8H_{16}O_4$	9.06	1.17
$C_8H_{18}NO_3$	9.43	1.00
$C_8H_{20}N_2O_2$	9.81	0.83
$C_8H_4O_4$	9.95	1.24
$C_8H_6NO_3$	10.32	1.08
$C_8H_8N_2O_2$	10.70	0.92
$C_8H_{10}N_3O$	11.07	0.76
$C_8H_{12}N_4$	11.44	0.60
$C_8H_{10}O_3$	10.16	1.07
$C_{10}H_6O_3$	11.05	1.15
$C_{10}H_8NO_2$	11.43	0.99
$C_{10}H_{12}N_2O$	11.80	0.84

	P + 1	P + 2
$C_{10}H_{14}N_3$	12.17	0.68
$C_{11}H_2N_3$	13.06	0.79
$C_{11}H_{12}O_2$	12.16	1.08
$C_{11}H_{14}NO$	12.53	0.92
$C_{11}H_{16}N_2$	12.91	0.77
$C_{12}H_2NO$	13.42	1.03
$C_{12}H_4N_2$	13.79	0.88
$C_{12}H_{16}O$	13.26	1.01
$C_{12}H_{18}N$	13.64	0.86
$C_{13}H_4O$	14.15	1.13
$C_{13}H_6N$	14.53	0.98
$C_{13}H_{20}$	14.37	0.96
$C_{14}H_8$	15.26	1.08
177		
$C_6H_{13}N_2O_4$	7.61	1.06
$C_6H_{15}N_3O_3$	7.99	0.88
$C_6H_{17}N_4O_2$	8.36	0.71
C_7HNO_4	8.50	1.12
$C_7H_3N_2O_3$	8.87	0.95
$C_7H_5N_4O_2$	9.25	0.78
$C_7H_5NO_4$	8.34	1.11
$C_7H_{17}N_2O_3$	8.72	0.94
$C_7H_{19}N_3O_2$	9.09	0.77
$C_8H_5NO_4$	9.23	1.18
$C_8H_7N_2O_3$	9.61	1.01
$C_8H_9N_4O_2$	9.98	0.85
$C_8H_9N_4O$	10.35	0.69
$C_8H_{17}O_4$	9.07	1.17
$C_8H_{19}NO_3$	9.45	1.00
$C_8H_5O_4$	9.96	1.25
$C_8H_7NO_3$	10.34	1.08
$C_8H_9N_2O_2$	10.71	0.92
$C_8H_{11}N_3O$	11.09	0.76
$C_8H_{13}N_4$	11.46	0.60
$C_{10}HN_4$	12.35	0.70
$C_{10}H_9O_3$	11.07	1.16
$C_{10}H_{11}NO_2$	11.44	1.00
$C_{10}H_{13}N_2O$	11.82	0.84
$C_{10}H_{15}N_3$	12.19	0.68
$C_{11}HN_2O$	12.71	0.94
$C_{11}H_3N_3$	13.08	0.79
$C_{11}H_{13}O_2$	12.17	1.08
$C_{11}H_{15}NO$	12.55	0.92
$C_{11}H_{17}N_2$	12.92	0.77
$C_{12}HO_2$	13.06	1.18
$C_{12}H_3NO$	13.44	1.03
$C_{12}H_5N_2$	13.81	0.88
$C_{12}H_{17}O$	13.28	1.01
$C_{12}H_{19}N$	13.65	0.86
$C_{13}H_5O$	14.17	1.13
$C_{13}H_7N$	14.54	0.98
$C_{13}H_{21}$	14.38	0.96
$C_{14}H_9$	15.27	1.08
178		
$C_6H_{14}N_2O_4$	7.63	1.06
$C_6H_{16}N_3O_3$	8.00	0.88
$C_6H_{18}N_4O_2$	8.38	0.71
$C_7H_2N_2O_4$	8.52	1.12
$C_7H_4N_3O_3$	8.89	0.95
$C_7H_6N_4O_2$	9.26	0.79
$C_7H_{16}NO_4$	8.36	1.11

	P + 1	P + 2
$C_7H_{18}N_2O_3$	8.73	0.94
$C_8H_4NO_4$	9.25	1.18
$C_8H_6N_2O_3$	9.62	1.02
$C_8H_8N_4O_2$	10.00	0.85
$C_8H_{16}N_4O$	10.37	0.69
$C_8H_{18}O_4$	9.09	1.17
$C_8H_6O_4$	9.98	1.25
$C_8H_8NO_3$	10.35	1.08
$C_8H_{10}N_2O_2$	10.73	0.92
$C_8H_{12}N_3O$	11.10	0.76
$C_8H_{14}N_4$	11.48	0.60
$C_{10}H_2N_4$	12.36	0.70
$C_{10}H_{10}O_3$	11.08	1.16
$C_{10}H_{12}NO_2$	11.46	1.00
$C_{10}H_{14}N_2O$	11.83	0.84
$C_{10}H_{16}N_3$	12.21	0.68
$C_{11}H_4N_2O$	12.72	0.94
$C_{11}H_6N_3$	13.10	0.79
$C_{11}H_{14}O_2$	12.19	1.08
$C_{11}H_{16}NO$	12.56	0.92
$C_{11}H_{18}N_2$	12.94	0.77
$C_{12}H_2O_2$	13.08	1.19
$C_{12}H_4NO$	13.45	1.03
$C_{12}H_6N_2$	13.83	0.88
$C_{12}H_{18}O$	13.29	1.01
$C_{12}H_{20}N$	13.67	0.86
$C_{13}H_6O$	14.18	1.13
$C_{13}H_8N$	14.56	0.98
$C_{13}H_{22}$	14.40	0.96
$C_{14}H_{10}$	15.29	1.09
179		
$C_6H_{15}N_2O_4$	7.64	1.06
$C_6H_{17}N_3O_3$	8.02	0.89
$C_7H_3N_2O_4$	8.53	1.12
$C_7H_5N_3O_3$	8.91	0.95
$C_7H_7N_4O_2$	9.28	0.79
$C_7H_7NO_4$	8.37	1.11
$C_8H_5NO_4$	9.26	1.18
$C_8H_7N_2O_3$	9.64	1.02
$C_8H_9N_3O_2$	10.01	0.85
$C_8H_{11}N_4O$	10.39	0.69
$C_8H_7O_4$	9.99	1.25
$C_8H_9NO_3$	10.37	1.09
$C_8H_{11}N_2O_2$	10.74	0.92
$C_8H_{13}N_3O$	11.12	0.76
$C_8H_{15}N_4$	11.49	0.60
$C_{10}HN_2O$	12.01	0.86
$C_{10}H_3N_4$	12.38	0.71
$C_{10}H_{11}O_3$	11.10	1.16
$C_{10}H_{13}NO_2$	11.47	1.00
$C_{10}H_{15}N_2O$	11.85	0.84
$C_{10}H_{17}N_3$	12.22	0.69
$C_{11}HNO_2$	12.36	1.10
$C_{11}H_5N_2O$	12.74	0.95
$C_{11}H_7N_3$	13.11	0.79
$C_{11}H_{15}O_2$	12.21	1.08
$C_{11}H_{17}NO$	12.58	0.93
$C_{11}H_{19}N_2$	12.95	0.77
$C_{12}H_3O_2$	13.09	1.19
$C_{12}H_5NO$	13.47	1.04
$C_{12}H_7N_2$	13.84	0.89
$C_{12}H_{19}O$	13.31	1.02

	P + 1	P + 2
$C_{12}H_{21}N$	13.69	0.87
$C_{13}H_7O$	14.20	1.13
$C_{13}H_9N$	14.57	0.99
$C_{13}H_{23}$	14.42	0.96
$C_{14}H_{11}$	15.30	1.09
180		
$C_6H_{16}N_2O_4$	7.66	1.06
$C_7H_4N_2O_4$	8.55	1.12
$C_7H_6N_3O_3$	8.92	0.96
$C_7H_8N_4O_2$	9.30	0.79
$C_8H_8NO_4$	9.28	1.18
$C_8H_8N_2O_3$	9.65	1.02
$C_8H_{10}N_3O_2$	10.03	0.85
$C_8H_{12}N_4O$	10.40	0.69
$C_8H_{20}O_4$	10.01	1.25
$C_8H_{10}NO_3$	10.38	1.09
$C_8H_{12}N_2O_2$	10.76	0.93
$C_8H_{14}N_3O$	11.13	0.77
$C_8H_{16}N_4$	11.51	0.61
$C_{10}H_2N_3O$	12.02	0.86
$C_{10}H_4N_4$	12.40	0.71
$C_{10}H_{12}O_3$	11.12	1.16
$C_{10}H_{14}NO_2$	11.49	1.00
$C_{10}H_{16}N_2O$	11.86	0.84
$C_{10}H_{18}N_3$	12.24	0.69
$C_{11}H_2NO_2$	12.38	1.10
$C_{11}H_4N_2O$	12.75	0.95
$C_{11}H_6N_3$	13.13	0.80
$C_{11}H_{16}O_2$	12.22	1.08
$C_{11}H_{18}NO$	12.60	0.93
$C_{11}H_{20}N_2$	12.97	0.78
$C_{12}H_4O_2$	13.11	1.19
$C_{12}H_6NO$	13.48	1.04
$C_{12}H_8N_2$	13.86	0.89
$C_{12}H_{20}O$	13.33	1.02
$C_{12}H_{22}N$	13.70	0.87
$C_{13}H_8O$	14.22	1.13
$C_{13}H_{10}N$	14.59	0.99
$C_{13}H_{24}$	14.43	0.97
$C_{14}H_{12}$	15.32	1.09
181		
$C_7H_5N_2O_4$	8.56	1.13
$C_7H_7N_3O_3$	8.94	0.96
$C_7H_9N_4O_2$	9.31	0.79
$C_8H_7NO_4$	9.30	1.19
$C_8H_9N_2O_3$	9.67	1.02
$C_8H_{11}N_3O_2$	10.04	0.86
$C_8H_{13}N_4O$	10.42	0.69
C_8HNO_4O	11.31	0.78
$C_8H_9O_4$	10.03	1.25
$C_8H_{11}NO_3$	10.40	1.09
$C_8H_{13}N_2O_2$	10.78	0.93
$C_8H_{15}N_3O$	11.15	0.77
$C_8H_{17}N_4$	11.52	0.61
$C_{10}HN_2O_2$	11.66	1.02
$C_{10}H_3N_2O$	12.04	0.86
$C_{10}H_5N_4$	12.41	0.71
$C_{10}H_{13}O_3$	11.13	1.16
$C_{10}H_{15}NO_2$	11.51	1.00
$C_{10}H_{17}N_2O$	11.88	0.85
$C_{10}H_{19}N_3$	12.25	0.69

	P + 1	P + 2
$C_{11}HO_3$	12.02	1.26
$C_{11}H_3NO_2$	12.39	1.10
$C_{11}H_5N_2O$	12.77	0.95
$C_{11}H_7N_3$	13.14	0.80
$C_{11}H_{17}O_2$	12.24	1.09
$C_{11}H_{19}NO$	12.61	0.93
$C_{11}H_{21}N_2$	12.99	0.78
$C_{12}H_5O_2$	13.13	1.19
$C_{12}H_7NO$	13.50	1.04
$C_{12}H_9N_2$	13.87	0.89
$C_{12}H_{21}O$	13.34	1.02
$C_{12}H_{23}N$	13.72	0.87
$C_{13}H_9O$	14.23	1.14
$C_{13}H_{11}N$	14.61	0.99
$C_{13}H_{25}$	14.45	0.97
$C_{14}H_{13}$	15.34	1.09
$C_{15}H$	16.23	1.23
182		
$C_7H_8N_2O_4$	8.58	1.13
$C_7H_8N_6O_3$	8.95	0.96
$C_7H_8N_4O_2$	9.33	0.79
$C_8H_8NO_4$	9.31	1.19
$C_8H_{10}N_2O_3$	9.69	1.02
$C_8H_{12}N_2O_2$	10.06	0.86
$C_8H_{14}N_4O$	10.43	0.70
$C_8H_2N_6O$	11.32	0.79
$C_8H_{16}O_4$	10.04	1.25
$C_9H_{12}NO_3$	10.42	1.09
$C_9H_{14}N_2O_2$	10.79	0.93
$C_9H_{16}N_2O$	11.17	0.77
$C_9H_{18}N_4$	11.54	0.61
$C_{10}H_2N_2O_2$	11.68	1.02
$C_{10}H_4N_2O$	12.05	0.87
$C_{10}H_6N_4$	12.43	0.71
$C_{10}H_{14}O_3$	11.15	1.16
$C_{10}H_{16}NO_2$	11.52	1.01
$C_{10}H_{18}N_2O$	11.90	0.85
$C_{10}H_{20}N_3$	12.27	0.69
$C_{11}H_2O_3$	12.04	1.26
$C_{11}H_4NO_2$	12.41	1.11
$C_{11}H_6N_2O$	12.79	0.95
$C_{11}H_8N_4$	13.16	0.80
$C_{11}H_{16}O_2$	12.25	1.09
$C_{11}H_{18}NO$	12.63	0.93
$C_{11}H_{20}N_2$	13.00	0.78
$C_{12}H_8O_2$	13.14	1.19
$C_{12}H_{10}NO$	13.52	1.04
$C_{12}H_{12}N_2$	13.89	0.89
$C_{12}H_{22}O$	13.36	1.02
$C_{12}H_{24}N$	13.73	0.87
$C_{13}H_{16}O$	14.25	1.14
$C_{13}H_{17}N$	14.62	0.99
$C_{13}H_{28}$	14.46	0.97
$C_{14}H_{14}$	15.35	1.10
$C_{15}H_2$	16.24	1.21
183		
$C_7H_7N_2O_4$	8.60	1.13
$C_7H_9N_5O_3$	8.97	0.96
$C_7H_{11}N_4O_2$	9.34	0.79
$C_8H_9NO_4$	9.33	1.19
$C_8H_{11}N_2O_3$	9.70	1.02
$C_8H_{13}N_3O_2$	10.08	0.86
$C_8H_{15}N_4O$	10.45	0.70
$C_8HN_3O_2$	10.96	0.95
$C_8H_3N_4O$	11.34	0.79
$C_8H_{17}O_4$	10.06	1.26
$C_9H_{13}NO_3$	10.43	1.09
$C_9H_{15}N_2O_2$	10.81	0.93
$C_9H_{17}N_2O$	11.18	0.77
$C_9H_{19}N_4$	11.56	0.61
$C_{10}HNO_3$	11.32	1.18
$C_{10}H_3N_2O_2$	11.70	1.03
$C_{10}H_5N_2O$	12.07	0.87
$C_{10}H_7N_4$	12.44	0.71
$C_{10}H_{15}O_3$	11.16	1.17
$C_{10}H_{17}NO_2$	11.54	1.01
$C_{10}H_{19}N_2O$	11.91	0.85
$C_{10}H_{21}N_3$	12.29	0.69
$C_{11}H_3O_3$	12.05	1.26
$C_{11}H_5NO_2$	12.43	1.11
$C_{11}H_7N_2O$	12.80	0.95
$C_{11}H_9N_3$	13.18	0.80
$C_{11}H_{17}O_2$	12.27	1.09
$C_{11}H_{19}NO$	12.64	0.93
$C_{11}H_{21}N_2$	13.02	0.78
$C_{12}H_7O_2$	13.16	1.20
$C_{12}H_9NO$	13.53	1.05
$C_{12}H_{11}N_2$	13.91	0.90
$C_{12}H_{23}O$	13.37	1.02
$C_{12}H_{25}N$	13.75	0.87
$C_{13}H_{11}O$	14.26	1.14
$C_{13}H_{13}N$	14.64	0.99
$C_{13}H_{27}$	14.48	0.97
$C_{14}HN$	15.53	1.12
$C_{14}H_{15}$	15.37	1.10
$C_{15}H_3$	16.26	1.23
184		
$C_7H_8N_2O_4$	8.61	1.13
$C_7H_{10}N_6O_3$	8.99	0.96
$C_7H_{12}N_4O_2$	9.36	0.80
$C_8H_{10}NO_4$	9.34	1.19
$C_8H_{12}N_2O_3$	9.72	1.03
$C_8H_{14}N_2O_2$	10.09	0.86
$C_8H_{16}N_4O$	10.47	0.70
$C_8H_2N_6O_2$	10.98	0.95
$C_8H_4N_4O$	11.35	0.79
$C_9H_{12}O_4$	10.07	1.26
$C_9H_{14}NO_3$	10.45	1.09
$C_9H_{16}N_2O_2$	10.82	0.93
$C_9H_{18}N_3O$	11.20	0.77
$C_9H_{20}N_4$	11.57	0.61
$C_{10}H_2NO_3$	11.34	1.18
$C_{10}H_4N_2O_2$	11.71	1.03
$C_{10}H_6N_3O$	12.09	0.87
$C_{10}H_8N_4$	12.46	0.71
$C_{10}H_{16}O_3$	11.18	1.17
$C_{10}H_{18}NO_2$	11.55	1.01
$C_{10}H_{20}N_2O$	11.93	0.85
$C_{10}H_{22}N_3$	12.30	0.70
$C_{11}H_4O_3$	12.07	1.27
$C_{11}H_6NO_2$	12.44	1.11
$C_{11}H_8N_2O$	12.82	0.96
$C_{11}H_{10}N_3$	13.19	0.80
$C_{11}H_{20}O_2$	12.29	1.09
$C_{11}H_{22}NO$	12.66	0.94
$C_{11}H_{24}N_2$	13.03	0.78
$C_{12}H_8O_2$	13.17	1.20
$C_{12}H_{10}NO$	13.55	1.05
$C_{12}H_{12}N_2$	13.92	0.90
$C_{12}H_{24}O$	13.39	1.03
$C_{12}H_{26}N$	13.77	0.88
$C_{13}H_{12}O$	14.28	1.14
$C_{13}H_{14}N$	14.65	1.00
$C_{13}H_{28}$	14.50	0.97
$C_{14}H_2N$	15.54	1.13
$C_{14}H_{16}$	15.38	1.10
$C_{15}H_4$	16.27	1.24
185		
$C_7H_9N_2O_4$	8.63	1.13
$C_7H_{11}N_5O_3$	9.00	0.96
$C_7H_{13}N_4O_2$	9.38	0.80
$C_8HN_4O_2$	10.27	0.88
$C_8H_{11}NO_4$	9.36	1.19
$C_8H_{13}N_2O_3$	9.73	1.03
$C_8H_{15}N_2O_2$	10.11	0.86
$C_8H_{17}N_4O$	10.48	0.70
$C_8HN_2O_3$	10.62	1.11
$C_8H_3N_2O_2$	11.00	0.95
$C_8H_5N_4O$	11.37	0.79
$C_8H_{13}O_4$	10.09	1.26
$C_8H_{15}NO_3$	10.46	1.10
$C_8H_{17}N_2O_2$	10.84	0.93
$C_8H_{19}N_3O$	11.21	0.77
$C_8H_{21}N_4$	11.59	0.62
C_9HO_4	10.98	1.35
$C_9H_3NO_3$	11.35	1.19
$C_9H_5N_2O_2$	11.73	1.03
$C_9H_7N_3O$	12.10	0.87
$C_9H_9N_4$	12.48	0.72
$C_9H_{17}O_3$	11.20	1.17
$C_9H_{19}NO_2$	11.57	1.01
$C_9H_{21}N_2O$	11.94	0.85
$C_9H_{23}N_3$	12.32	0.70
$C_{11}H_5O_2$	12.08	1.27
$C_{11}H_7NO_2$	12.46	1.11
$C_{11}H_9N_2O$	12.83	0.96
$C_{11}H_{11}N_3$	13.21	0.81
$C_{11}H_{21}O_2$	12.30	1.09
$C_{11}H_{23}NO$	12.68	0.94
$C_{11}H_{25}N_2$	13.05	0.79
$C_{12}H_9O_2$	13.19	1.20
$C_{12}H_{11}NO$	13.56	1.05
$C_{12}H_{13}N_2$	13.94	0.90
$C_{12}H_{25}O$	13.41	1.03
$C_{12}H_{27}N$	13.78	0.88
$C_{13}HN_2$	14.83	1.02
$C_{13}H_{13}O$	14.30	1.15
$C_{13}H_{15}N$	14.67	1.00
$C_{14}HO$	15.18	1.27
$C_{14}H_3N$	15.56	1.13
$C_{14}H_{17}$	15.40	1.10
$C_{15}H_5$	16.29	1.24
186		
$C_7H_{10}N_2O_4$	8.64	1.13
$C_7H_{12}N_6O_3$	9.02	0.97
$C_7H_{14}N_4O_2$	9.39	0.80
$C_8H_2N_4O_2$	10.28	0.88
$C_8H_{12}NO_4$	9.38	1.19
$C_8H_{14}N_2O_3$	9.75	1.03
$C_8H_{16}N_2O_2$	10.12	0.86
$C_8H_{18}N_4O$	10.50	0.70
$C_8H_4N_2O_3$	10.64	1.11
$C_8H_6N_4O_2$	11.01	0.95
$C_8H_8N_4O$	11.39	0.79
$C_8H_{14}O_4$	10.11	1.26
$C_9H_{16}NO_3$	10.48	1.10
$C_9H_{18}N_2O_2$	10.86	0.94
$C_9H_{20}N_3O$	11.23	0.78
$C_9H_{22}N_4$	11.60	0.62
$C_{10}H_2O_4$	10.99	1.35
$C_{10}H_4NO_3$	11.37	1.19
$C_{10}H_6N_2O_2$	11.74	1.03
$C_{10}H_8N_3O$	12.12	0.87
$C_{10}H_{10}N_4$	12.49	0.72
$C_{10}H_{18}O_3$	11.21	1.17
$C_{10}H_{20}NO_2$	11.59	1.01
$C_{10}H_{22}N_2O$	11.96	0.86
$C_{10}H_{24}N_3$	12.33	0.70
$C_{11}H_6O_3$	12.10	1.27
$C_{11}H_8NO_2$	12.47	1.11
$C_{11}H_{10}N_2O$	12.85	0.96
$C_{11}H_{12}N_3$	13.22	0.81
$C_{11}H_{22}O_2$	12.32	1.10
$C_{11}H_{24}NO$	12.69	0.94
$C_{11}H_{26}N_2$	13.07	0.79
$C_{12}H_{10}O_2$	13.21	1.20
$C_{12}H_{12}NO$	13.58	1.05
$C_{12}H_{14}N_2$	13.95	0.90
$C_{12}H_{26}O$	13.42	1.03
$C_{13}H_2N_2$	14.84	1.02
$C_{13}H_{14}O$	14.31	1.15
$C_{13}H_{16}N$	14.69	1.00
$C_{14}H_2O$	15.20	1.27
$C_{14}H_4N$	15.57	1.13
$C_{14}H_{18}$	15.42	1.11
$C_{15}H_6$	16.31	1.24
187		
$C_7H_{11}N_2O_4$	8.66	1.13
$C_7H_{13}N_5O_3$	9.03	0.97
$C_7H_{15}N_4O_2$	9.41	0.80
$C_8HN_3O_3$	9.92	1.04
$C_8H_3N_4O_2$	10.30	0.88
$C_8H_{15}NO_4$	9.39	1.20
$C_8H_{17}N_2O_3$	9.77	1.03
$C_8H_{17}N_3O_2$	10.14	0.87
$C_8H_{19}N_4O$	10.51	0.70
$C_8H_5NO_4$	10.28	1.28
$C_8H_7N_2O_3$	10.65	1.11
$C_8H_9N_3O_2$	11.03	0.95
$C_8H_{11}N_4O$	11.40	0.80
$C_8H_{15}O_4$	10.12	1.26
$C_8H_{17}NO_3$	10.50	1.10
$C_8H_{19}N_2O_2$	10.87	0.94
$C_8H_{21}N_3O$	11.25	0.78
$C_8H_{23}N_4$	11.62	0.62
$C_{10}H_3O_4$	11.01	1.35
$C_{10}H_5NO_3$	11.39	1.19

	P + 1	P + 2
$C_{16}H_{17}N_2O_2$	11.76	1.03
$C_{16}H_{18}N_3O$	12.13	0.88
$C_{16}H_{11}N_4$	12.51	0.72
$C_{16}H_{19}O_2$	11.23	1.17
$C_{16}H_{21}NO_2$	11.60	1.01
$C_{16}H_{23}N_2O$	11.98	0.86
$C_{16}H_{25}N_3$	12.35	0.70
$C_{11}H_7O_3$	12.12	1.27
$C_{11}H_8NO_2$	12.49	1.12
$C_{11}H_{11}N_2O$	12.87	0.96
$C_{11}H_{13}N_3$	13.24	0.81
$C_{11}H_{25}O_2$	12.33	1.10
$C_{11}H_{27}NO$	12.71	0.94
$C_{12}HN_3$	14.13	0.93
$C_{12}H_{11}O_2$	13.22	1.20
$C_{12}H_{13}NO$	13.60	1.05
$C_{12}H_{15}N_2$	13.97	0.90
$C_{13}HNO$	14.48	1.17
$C_{13}H_3N_2$	14.86	1.03
$C_{13}H_{15}O$	14.33	1.15
$C_{13}H_{17}N$	14.70	1.00
$C_{14}H_5O$	15.22	1.28
$C_{14}H_7N$	15.59	1.13
$C_{14}H_{18}$	15.43	1.11
$C_{15}H_7$	16.32	1.24
188		
$C_7H_{12}N_2O_4$	8.68	1.14
$C_7H_{14}N_3O_3$	9.05	0.97
$C_7H_{16}N_4O_2$	9.42	0.80
$C_8H_{12}N_2O_3$	9.94	1.05
$C_8H_{14}N_4O_2$	10.31	0.88
$C_8H_{14}NO_4$	9.41	1.20
$C_8H_{16}N_2O_3$	9.78	1.03
$C_8H_{18}N_3O_2$	10.16	0.87
$C_8H_{20}N_4O$	10.53	0.71
$C_9H_2NO_4$	10.30	1.28
$C_9H_4N_2O_3$	10.67	1.12
$C_9H_6N_3O_2$	11.04	0.96
$C_9H_8N_4O$	11.42	0.80
$C_9H_{16}O_4$	10.14	1.26
$C_9H_{18}NO_3$	10.51	1.10
$C_9H_{20}N_2O_2$	10.89	0.94
$C_9H_{22}N_3O$	11.26	0.78
$C_9H_{24}N_4$	11.64	0.62
$C_{10}H_4O_4$	11.03	1.35
$C_{10}H_6NO_3$	11.40	1.19
$C_{10}H_8N_2O_2$	11.78	1.03
$C_{10}H_{10}N_3O$	12.15	0.88
$C_{10}H_{12}N_4$	12.52	0.72
$C_{10}H_{20}O_3$	11.24	1.18
$C_{10}H_{22}NO_2$	11.62	1.02
$C_{10}H_{24}N_2O$	11.99	0.86
$C_{11}H_9O_3$	12.13	1.27
$C_{11}H_{19}NO_2$	12.51	1.12
$C_{11}H_{12}N_2O$	12.88	0.96
$C_{11}H_{14}N_3$	13.26	0.81
$C_{11}H_{26}O_2$	12.35	1.10
$C_{12}H_2N_3$	14.14	0.93
$C_{12}H_{12}O_2$	13.24	1.21
$C_{12}H_{14}NO$	13.61	1.06
$C_{12}H_{16}N_2$	13.99	0.91
$C_{13}H_2NO$	14.50	1.18
$C_{13}H_4N_2$	14.88	1.03
$C_{13}H_{16}O$	14.34	1.15
$C_{13}H_{18}N$	14.72	1.01
$C_{14}H_4O$	15.23	1.28
$C_{14}H_6N$	15.61	1.14
$C_{14}H_{20}$	15.45	1.11
$C_{15}H_8$	16.34	1.25
189		
$C_7H_{13}N_2O_4$	8.69	1.14
$C_7H_{15}N_3O_3$	9.07	0.97
$C_7H_{17}N_4O_2$	9.44	0.80
$C_8HN_2O_4$	9.58	1.21
$C_8H_3N_3O_3$	9.95	1.05
$C_8H_5N_4O_2$	10.33	0.88
$C_8H_{15}NO_4$	9.42	1.20
$C_8H_{17}N_2O_3$	9.80	1.03
$C_8H_{19}N_3O_2$	10.17	0.87
$C_8H_{21}N_4O$	10.55	0.71
$C_9H_5NO_4$	10.31	1.28
$C_9H_7N_2O_3$	10.69	1.12
$C_9H_9N_3O_2$	11.06	0.96
$C_9H_{11}N_4O$	11.43	0.80
$C_9H_{17}O_4$	10.15	1.26
$C_9H_{19}NO_3$	10.53	1.10
$C_9H_{21}N_2O_2$	10.90	0.94
$C_9H_{23}N_3O$	11.28	0.78
$C_{10}H_5O_4$	11.04	1.35
$C_{10}H_7NO_3$	11.42	1.19
$C_{10}H_9N_2O_2$	11.79	1.04
$C_{10}H_{11}N_3O$	12.17	0.88
$C_{10}H_{13}N_4$	12.54	0.72
$C_{10}H_{21}O_3$	11.26	1.18
$C_{10}H_{23}NO_2$	11.63	1.02
$C_{11}HN_4$	13.43	0.83
$C_{11}H_9O_3$	12.15	1.28
$C_{11}H_{11}NO_2$	12.52	1.12
$C_{11}H_{13}N_2O$	12.90	0.97
$C_{11}H_{15}N_3$	13.27	0.81
$C_{12}HN_2O$	13.79	1.08
$C_{12}H_3N_3$	14.16	0.93
$C_{12}H_{13}O_2$	13.25	1.21
$C_{12}H_{15}NO$	13.63	1.06
$C_{12}H_{17}N_2$	14.00	0.91
$C_{13}HO_2$	14.14	1.33
$C_{13}H_3NO$	14.52	1.18
$C_{13}H_5N_2$	14.89	1.03
$C_{13}H_{17}O$	14.36	1.16
$C_{13}H_{19}N$	14.73	1.01
$C_{14}H_3O$	15.25	1.28
$C_{14}H_7N$	15.62	1.14
$C_{14}H_{21}$	15.46	1.11
$C_{15}H_9$	16.35	1.25
190		
$C_7H_{14}N_2O_4$	8.71	1.14
$C_7H_{16}N_3O_3$	9.08	0.97
$C_7H_{18}N_4O_2$	9.46	0.80
$C_8H_2N_2O_4$	9.60	1.21
$C_8H_4N_3O_3$	9.97	1.05
$C_8H_6N_4O_2$	10.35	0.89
$C_8H_{16}NO_4$	9.44	1.20
$C_8H_{18}N_2O_3$	9.81	1.03
$C_8H_{20}N_3O_2$	10.19	0.87
$C_8H_{22}N_4O$	10.56	0.71
$C_9H_4NO_4$	10.33	1.28
$C_9H_6N_2O_3$	10.70	1.12
$C_9H_8N_3O_2$	11.08	0.96
$C_9H_{10}N_4O$	11.45	0.80
$C_9H_{18}O_4$	10.17	1.27
$C_9H_{20}NO_3$	10.54	1.10
$C_9H_{22}N_2O_2$	10.92	0.94
$C_9H_{24}N_3O$	11.06	1.35
$C_{10}H_6O_4$	11.43	1.20
$C_{10}H_8NO_3$	11.81	1.03
$C_{10}H_{10}N_2O_2$	12.18	0.88
$C_{10}H_{12}N_3O$	12.56	0.73
$C_{10}H_{14}N_4$	12.93	0.57
$C_{10}H_{22}O_3$	11.28	1.18
$C_{11}H_2N_4$	13.44	0.84
$C_{11}H_{10}O_3$	12.16	1.28
$C_{11}H_{12}NO_2$	12.54	1.12
$C_{11}H_{14}N_2O$	12.91	0.97
$C_{11}H_{16}N_3$	13.29	0.82
$C_{12}H_2N_2O$	13.80	1.08
$C_{12}H_4N_3$	14.18	0.93
$C_{12}H_{14}O_2$	13.27	1.21
$C_{12}H_{16}NO$	13.64	1.06
$C_{12}H_{18}N_2$	14.02	0.91
$C_{13}H_2O_2$	14.16	1.33
$C_{13}H_4NO$	14.53	1.18
$C_{13}H_6N_2$	14.91	1.03
$C_{13}H_{18}O$	14.38	1.16
$C_{13}H_{20}N$	14.75	1.01
$C_{14}H_6O$	15.26	1.28
$C_{14}H_8N$	15.64	1.14
$C_{14}H_{22}$	15.48	1.12
$C_{15}H_{10}$	16.37	1.25
191		
$C_7H_{11}N_2O_4$	8.72	1.14
$C_7H_{13}N_3O_3$	9.10	0.97
$C_7H_{15}N_4O_2$	9.47	0.81
$C_8H_3N_2O_4$	9.61	1.22
$C_8H_5N_3O_3$	9.99	1.05
$C_8H_7N_4O_2$	10.36	0.89
$C_8H_{17}NO_4$	9.46	1.20
$C_8H_{19}N_2O_3$	9.83	1.04
$C_8H_{21}N_3O_2$	10.20	0.87
$C_8H_{23}NO_4$	10.34	1.28
$C_9H_7NO_4$	10.72	1.12
$C_9H_9N_2O_3$	11.09	0.96
$C_9H_{11}N_4O$	11.47	0.80
$C_9H_{19}O_4$	10.19	1.27
$C_9H_{21}NO_3$	10.56	1.11
$C_{10}H_7O_4$	11.07	1.36
$C_{10}H_9NO_3$	11.45	1.20
$C_{10}H_{11}N_2O_2$	11.82	1.04
$C_{10}H_{13}N_3O$	12.20	0.88
$C_{10}H_{15}N_4$	12.57	0.73
$C_{11}HN_3O$	13.09	0.99
$C_{11}H_3N_4$	13.46	0.84
$C_{11}H_{11}O_3$	12.18	1.28
$C_{11}H_{13}NO_2$	12.55	1.12
$C_{11}H_{15}N_2O$	12.93	0.97
$C_{11}H_{17}N_3$	13.30	0.82
$C_{12}HNO_2$	13.44	1.23
$C_{12}H_3N_2O$	13.82	1.08
$C_{12}H_5N_3$	14.19	0.93
$C_{12}H_{15}O_2$	13.29	1.21
$C_{12}H_{17}NO$	13.66	1.06
$C_{12}H_{19}N_2$	14.03	0.91
$C_{13}H_5O_2$	14.17	1.33
$C_{13}H_7NO$	14.55	1.18
$C_{13}H_9N_2$	14.92	1.04
$C_{13}H_{19}O$	14.39	1.16
$C_{13}H_{21}N$	14.77	1.01
$C_{14}H_9O$	15.28	1.29
$C_{14}H_{23}N$	15.65	1.14
$C_{14}H_{23}$	15.50	1.12
$C_{15}H_{11}$	16.39	1.25
192		
$C_7H_{16}N_2O_4$	8.74	1.14
$C_7H_{18}N_3O_3$	9.11	0.97
$C_7H_{20}N_4O_2$	9.49	0.81
$C_8H_4N_2O_4$	9.63	1.22
$C_8H_6N_3O_3$	10.00	1.05
$C_8H_8N_4O_2$	10.38	0.89
$C_8H_{18}NO_4$	9.47	1.20
$C_8H_{20}N_2O_3$	9.85	1.04
$C_8H_{22}NO_4$	10.36	1.29
$C_9H_8N_2O_3$	10.73	1.12
$C_9H_{10}N_3O_2$	11.11	0.96
$C_9H_{12}N_4O$	11.48	0.80
$C_9H_{20}O_4$	10.20	1.27
$C_9H_{22}NO_3$	10.58	1.11
$C_{10}H_{10}NO_3$	11.47	1.20
$C_{10}H_{12}N_2O_2$	11.84	1.04
$C_{10}H_{14}N_3O$	12.21	0.89
$C_{10}H_{16}N_4$	12.59	0.73
$C_{11}H_2N_3O$	13.10	0.99
$C_{11}H_4N_4$	13.48	0.84
$C_{11}H_{12}O_3$	12.20	1.28
$C_{11}H_{14}NO_2$	12.57	1.13
$C_{11}H_{16}N_2O$	12.95	0.97
$C_{11}H_{18}N_3$	13.32	0.82
$C_{12}H_2NO_2$	13.46	1.24
$C_{12}H_4N_2O$	13.83	1.09
$C_{12}H_6N_3$	14.21	0.94
$C_{12}H_{16}O_2$	13.30	1.22
$C_{12}H_{18}NO$	13.68	1.06
$C_{12}H_{20}N_2$	14.05	0.92
$C_{13}H_4O_2$	14.19	1.33
$C_{13}H_6NO$	14.56	1.18
$C_{13}H_8N_2$	14.94	1.04
$C_{13}H_{20}O$	14.41	1.16
$C_{13}H_{22}N$	14.78	1.02
$C_{14}H_8O$	15.30	1.29
$C_{14}H_{10}N$	15.67	1.15
$C_{14}H_{24}$	15.51	1.12
$C_{15}H_{12}$	16.40	1.26
193		
$C_7H_{17}N_2O_4$	8.76	1.14
$C_7H_{19}N_3O_3$	9.13	0.98
$C_8H_5N_2O_4$	9.64	1.22
$C_8H_7N_3O_3$	10.02	1.05
$C_8H_9N_4O_2$	10.39	0.89
$C_8H_{19}NO_4$	9.49	1.20

	P + 1	P + 2
$C_4H_7NO_4$	10.38	1.29
$C_8H_9N_3O_3$	10.75	1.13
$C_8H_{11}N_2O_2$	11.12	0.96
$C_9H_{12}N_2O$	11.50	0.81
$C_{10}H_{14}O$	12.39	0.91
$C_{12}H_9O_4$	11.11	1.36
$C_{10}H_{11}NO_3$	11.48	1.20
$C_{11}H_{13}N_2O_2$	11.86	1.04
$C_{10}H_{15}N_2O$	12.23	0.89
$C_{11}H_{17}N_4$	12.60	0.73
$C_{11}H_{15}N_2O_2$	12.74	1.15
$C_{11}H_{13}N_2O$	13.12	0.99
$C_{11}H_{15}N_4$	13.49	0.84
$C_{11}H_{13}O_3$	12.21	1.28
$C_{11}H_{15}NO_2$	12.59	1.13
$C_{11}H_{17}N_2O$	12.96	0.97
$C_{11}H_{18}N_3$	13.34	0.82
$C_{12}HO_3$	13.10	1.39
$C_{12}H_{20}NO_2$	13.48	1.24
$C_{12}H_{22}N_2O$	13.85	1.09
$C_{12}H_{17}N_3$	14.22	0.94
$C_{12}H_{17}O_2$	13.32	1.22
$C_{12}H_{19}NO$	13.69	1.07
$C_{12}H_{21}N_2$	14.07	0.92
$C_{13}H_9O_2$	14.21	1.33
$C_{13}H_{17}NO$	14.58	1.19
$C_{13}H_{19}N_2$	14.96	1.04
$C_{13}H_{21}O$	14.42	1.16
$C_{13}H_{23}N$	14.80	1.02
$C_{14}H_{9}O$	15.31	1.29
$C_{14}H_{11}N$	15.69	1.15
$C_{14}H_{25}$	15.53	1.12
$C_{15}H_{13}$	16.42	1.26
$C_{16}H$	17.31	1.40
194		
$C_7H_{18}N_2O_4$	8.77	1.14
$C_8H_6N_2O_4$	9.66	1.22
$C_8H_8N_3O_3$	10.03	1.06
$C_8H_{10}N_4O_2$	10.41	0.89
$C_9H_8NO_4$	10.39	1.29
$C_9H_{10}N_2O_3$	10.77	1.13
$C_9H_{12}N_2O_2$	11.14	0.97
$C_9H_{14}N_4O$	11.51	0.81
$C_{10}H_8N_4O$	12.40	0.91
$C_{10}H_{10}O_4$	11.12	1.36
$C_{10}H_{12}NO_3$	11.50	1.20
$C_{10}H_{14}N_2O_2$	11.87	1.05
$C_{10}H_{16}N_2O$	12.25	0.89
$C_{10}H_{18}N_4$	12.62	0.74
$C_{11}H_{12}N_2O_2$	12.76	1.15
$C_{12}H_6N_4O$	13.13	1.00
$C_{12}H_8N_4$	13.51	0.85
$C_{11}H_{14}O_3$	12.23	1.28
$C_{11}H_{16}NO_2$	12.60	1.13
$C_{11}H_{18}N_2O$	12.98	0.98
$C_{11}H_{20}N_3$	13.35	0.82
$C_{12}H_8O_3$	13.12	1.39
$C_{12}H_{14}NO_2$	13.49	1.24
$C_{12}H_{16}N_2O$	13.87	1.09
$C_{12}H_{18}N_3$	14.24	0.94
$C_{12}H_{10}O_2$	13.33	1.22
$C_{12}H_{20}NO$	13.71	1.07
$C_{12}H_{22}N_2$	14.08	0.92
$C_{13}H_6O_2$	14.22	1.34
$C_{13}H_{18}NO$	14.60	1.19
$C_{13}H_{20}N_2$	14.97	1.04
$C_{13}H_{22}O$	14.44	1.17
$C_{13}H_{24}N$	14.81	1.02
$C_{14}H_{8}O$	15.33	1.29
$C_{14}H_{12}N$	15.70	1.15
$C_{14}H_{26}$	15.54	1.13
$C_{15}H_{14}$	16.43	1.26
$C_{16}H_2$	17.32	1.41
195		
$C_8H_7N_2O_4$	9.68	1.22
$C_8H_9N_3O_3$	10.05	1.06
$C_8H_{11}N_4O_2$	10.43	0.89
$C_9H_9NO_4$	10.41	1.29
$C_9H_{11}N_2O_3$	10.78	1.13
$C_9H_{13}N_2O_2$	11.16	0.97
$C_9H_{15}N_4O$	11.53	0.81
$C_{10}H_{11}N_2O_2$	12.05	1.07
$C_{10}H_{13}N_4O$	12.42	0.91
$C_{11}H_{11}O_4$	11.14	1.36
$C_{11}H_{13}NO_3$	11.51	1.21
$C_{11}H_{15}N_2O_2$	11.89	1.05
$C_{11}H_{17}N_2O$	12.26	0.89
$C_{11}H_{19}N_4$	12.64	0.74
$C_{11}HNO_3$	12.40	1.31
$C_{11}H_3N_2O_2$	12.78	1.15
$C_{11}H_{13}N_2O$	13.15	1.00
$C_{11}H_{15}N_4$	13.52	0.85
$C_{11}H_{13}O_3$	12.24	1.29
$C_{11}H_{17}NO_2$	12.62	1.13
$C_{11}H_{19}N_2O$	12.99	0.98
$C_{11}H_{21}N_3$	13.37	0.83
$C_{12}H_9O_3$	13.13	1.39
$C_{12}H_{15}NO_2$	13.51	1.24
$C_{12}H_{17}N_2O$	13.88	1.09
$C_{12}H_{19}N_3$	14.26	0.94
$C_{12}H_{11}O_2$	13.35	1.22
$C_{12}H_{21}NO$	13.72	1.07
$C_{12}H_{23}N_2$	14.10	0.92
$C_{13}H_7O_2$	14.24	1.34
$C_{13}H_9NO$	14.61	1.19
$C_{13}H_{11}N_2$	14.99	1.05
$C_{13}H_{23}O$	14.46	1.17
$C_{13}H_{25}N$	14.83	1.02
$C_{14}H_{11}O$	15.34	1.30
$C_{14}H_{13}N$	15.72	1.15
$C_{14}H_{27}$	15.56	1.13
$C_{15}HN$	16.61	1.29
$C_{15}H_{15}$	16.45	1.27
$C_{16}H_3$	17.34	1.41
196		
$C_8H_8N_2O_4$	9.69	1.22
$C_8H_{10}N_3O_3$	10.07	1.06
$C_8H_{12}N_4O_2$	10.44	0.90
$C_9H_{10}NO_4$	10.42	1.29
$C_9H_{12}N_2O_3$	10.80	1.13
$C_9H_{14}N_2O_2$	11.17	0.97
$C_9H_{16}N_4O$	11.55	0.81
$C_{10}H_{12}N_2O_2$	12.06	1.07
$C_{10}H_{14}N_4O$	12.44	0.91
$C_{10}H_{12}O_4$	11.15	1.37
$C_{10}H_{14}NO_3$	11.53	1.21
$C_{10}H_{16}N_2O_2$	11.90	1.05
$C_{10}H_{18}N_2O$	12.28	0.89
$C_{10}H_{20}N_4$	12.65	0.74
$C_{11}H_{14}NO_3$	12.42	1.31
$C_{11}H_{16}N_2O_2$	12.79	1.15
$C_{11}H_{18}N_2O$	13.17	1.00
$C_{11}H_{20}N_4$	13.54	0.85
$C_{11}H_{12}O_3$	12.26	1.29
$C_{11}H_{18}NO_2$	12.63	1.13
$C_{11}H_{20}N_2O$	13.01	0.98
$C_{11}H_{22}N_3$	13.38	0.83
$C_{12}H_8O_3$	13.15	1.40
$C_{12}H_{14}NO_2$	13.52	1.24
$C_{12}H_{16}N_2O$	13.90	1.09
$C_{12}H_{18}N_3$	14.27	0.95
$C_{12}H_{10}O_2$	13.37	1.22
$C_{12}H_{22}NO$	13.74	1.07
$C_{12}H_{24}N_2$	14.11	0.92
$C_{13}H_9O_2$	14.25	1.34
$C_{13}H_{10}NO$	14.63	1.19
$C_{13}H_{12}N_2$	15.00	1.05
$C_{13}H_{24}O$	14.47	1.17
$C_{13}H_{26}N$	14.85	1.03
$C_{14}H_{12}O$	15.36	1.30
$C_{14}H_{14}N$	15.73	1.16
$C_{14}H_{28}$	15.58	1.13
$C_{15}H_{16}N$	16.62	1.29
$C_{15}H_{16}$	16.47	1.27
$C_{16}H_4$	17.35	1.41
197		
$C_8H_9N_2O_4$	9.71	1.23
$C_8H_{11}N_3O_3$	10.08	1.06
$C_8H_{13}N_4O_2$	10.46	0.90
$C_9HN_4O_2$	11.35	0.99
$C_9H_{11}NO_4$	10.44	1.29
$C_9H_{13}N_2O_3$	10.81	1.13
$C_9H_{15}N_2O_2$	11.19	0.97
$C_9H_{17}N_4O$	11.56	0.81
$C_{10}HN_2O_3$	11.70	1.23
$C_{10}H_9N_2O_2$	12.08	1.07
$C_{10}H_{11}N_4O$	12.45	0.91
$C_{10}H_{13}O_4$	11.17	1.37
$C_{10}H_{15}NO_3$	11.55	1.21
$C_{10}H_{17}N_2O_2$	11.92	1.05
$C_{10}H_{19}N_2O$	12.29	0.90
$C_{10}H_{21}N_4$	12.67	0.74
$C_{11}HO_4$	12.06	1.46
$C_{11}H_3NO_3$	12.43	1.31
$C_{11}H_5N_2O_2$	12.81	1.16
$C_{11}H_7N_2O$	13.18	1.00
$C_{11}H_9N_4$	13.56	0.85
$C_{11}H_{17}O_3$	12.28	1.29
$C_{11}H_{19}NO_2$	12.65	1.14
$C_{11}H_{21}N_2O$	13.03	0.98
$C_{11}H_{23}N_3$	13.40	0.83
$C_{12}H_{11}O_3$	13.16	1.40
$C_{12}H_{17}NO_2$	13.54	1.25
$C_{12}H_{19}N_2O$	13.91	1.10
$C_{12}H_{11}N_3$	14.29	0.95
$C_{12}H_{21}O_2$	13.38	1.23
$C_{12}H_{23}NO$	13.76	1.08
$C_{12}H_{25}N_2$	14.13	0.93
$C_{13}H_9O_2$	14.27	1.34
$C_{13}H_{11}NO$	14.64	1.20
$C_{13}H_{13}N_2$	15.02	1.05
$C_{13}H_{25}O$	14.49	1.17
$C_{13}H_{27}N$	14.86	1.03
$C_{14}HN_2$	15.91	1.18
$C_{14}H_{13}O$	15.38	1.30
$C_{14}H_{15}N$	15.75	1.16
$C_{14}H_{29}$	15.59	1.13
$C_{15}HO$	16.26	1.44
$C_{15}H_3N$	16.64	1.30
$C_{15}H_{17}$	16.48	1.27
$C_{16}H_5$	17.37	1.42
198		
$C_8H_{10}N_2O_4$	9.72	1.23
$C_8H_{12}N_3O_3$	10.10	1.06
$C_8H_{14}N_4O_2$	10.47	0.90
$C_9H_2N_4O_2$	11.36	0.99
$C_9H_{12}NO_4$	10.46	1.30
$C_9H_{14}N_2O_3$	10.83	1.13
$C_9H_{16}N_2O_2$	11.20	0.97
$C_9H_{18}N_4O$	11.58	0.82
$C_{10}H_{14}N_2O_2$	11.72	1.23
$C_{10}H_{16}N_2O_2$	12.09	1.07
$C_{10}H_{18}N_4O$	12.47	0.92
$C_{10}H_{14}O_4$	11.19	1.37
$C_{10}H_{16}NO_3$	11.56	1.21
$C_{10}H_{18}N_2O_2$	11.94	1.05
$C_{10}H_{20}N_2O$	12.31	0.90
$C_{10}H_{22}N_4$	12.68	0.74
$C_{11}H_6O_4$	12.08	1.47
$C_{11}H_8NO_3$	12.45	1.31
$C_{11}H_{10}N_2O_2$	12.82	1.16
$C_{11}H_{12}N_2O$	13.20	1.01
$C_{11}H_{16}N_4$	13.57	0.85
$C_{11}H_{14}O_3$	12.29	1.29
$C_{11}H_{20}NO_2$	12.67	1.14
$C_{11}H_{22}N_2O$	13.04	0.99
$C_{11}H_{24}N_3$	13.42	0.83
$C_{12}H_{10}O_3$	13.18	1.40
$C_{12}H_{16}NO_2$	13.56	1.25
$C_{12}H_{18}N_2O$	13.93	1.10
$C_{12}H_{20}N_3$	14.30	0.95
$C_{12}H_{12}O_2$	13.40	1.23
$C_{12}H_{24}NO$	13.77	1.08
$C_{12}H_{26}N_2$	14.15	0.93
$C_{13}H_{14}O_2$	14.29	1.35
$C_{13}H_{26}NO$	14.66	1.20
$C_{13}H_{28}N_2$	15.04	1.05
$C_{14}H_{14}O$	14.50	1.18
$C_{14}H_{16}N$	14.88	1.03
$C_{14}H_{30}N_2$	15.92	1.18
$C_{14}H_{14}O$	15.39	1.30
$C_{14}H_{16}N$	15.77	1.16
$C_{14}H_{30}$	15.61	1.14
$C_{15}H_{30}$	16.28	1.44
$C_{15}H_{16}N$	16.65	1.30
$C_{15}H_{18}$	16.50	1.27
$C_{16}H_6$	17.39	1.42

	P + 1	P + 2
199		
$C_8H_{11}N_2O_4$	9.74	1.23
$C_9H_{13}N_3O_3$	10.11	1.06
$C_9H_{15}N_4O_2$	10.49	0.90
$C_9H_{17}N_5O_2$	11.00	1.15
$C_9H_{19}N_4O_2$	11.38	0.99
$C_9H_{19}NO_4$	10.47	1.30
$C_9H_{13}N_2O_3$	10.85	1.14
$C_9H_{17}N_2O_2$	11.22	0.98
$C_9H_{18}N_2O$	11.59	0.82
$C_{10}HNO_4$	11.36	1.39
$C_{10}H_3N_2O_2$	11.73	1.23
$C_{10}H_5N_3O_2$	12.11	1.07
$C_{10}H_7NO$	12.48	0.92
$C_{10}H_{13}O_4$	11.20	1.37
$C_{10}H_{17}NO_3$	11.58	1.21
$C_{10}H_{19}N_2O_2$	11.95	1.01
$C_{10}H_{21}N_2O$	12.33	0.90
$C_{10}H_{22}N_4$	12.70	0.75
$C_{11}H_3O_4$	12.09	1.47
$C_{11}H_5NO_3$	12.47	1.31
$C_{11}H_7N_2O_2$	12.84	1.16
$C_{11}H_9NO$	13.21	1.01
$C_{11}H_{11}N_4$	13.59	0.86
$C_{11}H_{19}O_3$	12.31	1.29
$C_{11}H_{21}NO_2$	12.68	1.14
$C_{11}H_{23}N_2O$	13.06	0.99
$C_{11}H_{25}N_3$	13.43	0.84
$C_{12}H_7O_3$	13.20	1.40
$C_{12}H_9NO_2$	13.57	1.25
$C_{12}H_{11}N_2O$	13.95	1.10
$C_{12}H_{13}N_3$	14.32	0.95
$C_{12}H_{23}O_2$	13.41	1.23
$C_{12}H_{25}NO$	13.79	1.08
$C_{12}H_{27}N_2$	14.16	0.93
$C_{13}HN_3$	15.21	1.08
$C_{13}H_{11}O_2$	14.30	1.35
$C_{13}H_{13}NO$	14.68	1.20
$C_{13}H_{15}N_2$	15.05	1.06
$C_{13}H_{27}O$	14.52	1.18
$C_{13}H_{29}N$	14.89	1.03
$C_{14}HNO$	15.57	1.33
$C_{14}H_3N_2$	15.94	1.19
$C_{14}H_{15}O$	15.41	1.31
$C_{14}H_{17}N$	15.78	1.16
$C_{15}H_9O$	16.30	1.44
$C_{15}H_{7}N$	16.67	1.30
$C_{15}H_{19}$	16.51	1.28
$C_{16}H_7$	17.40	1.42
200		
$C_8H_{12}N_2O_4$	9.76	1.23
$C_8H_{14}N_4O_3$	10.13	1.07
$C_8H_{16}N_4O_2$	10.51	0.90
$C_8H_{18}N_5O_2$	11.02	1.15
$C_8H_4N_4O_2$	11.39	0.99
$C_8H_{14}NO_4$	10.49	1.30
$C_8H_{16}N_2O_3$	10.86	1.14
$C_8H_{18}N_2O_2$	11.24	0.98
$C_8H_{20}N_4O$	11.61	0.82
$C_{10}H_2NO_4$	11.38	1.39
$C_{10}H_4N_2O_3$	11.75	1.23
$C_{10}H_6N_2O_2$	12.13	1.08
$C_{10}H_8N_4O$	12.50	0.92
$C_{10}H_{16}O_4$	11.22	1.37
$C_{10}H_{18}NO_3$	11.59	1.21
$C_{10}H_{20}N_2O_2$	11.97	1.06
$C_{10}H_{22}N_2O$	12.34	0.90
$C_{10}H_{24}N_4$	12.72	0.75
$C_{11}H_4O_4$	12.11	1.47
$C_{11}H_6NO_3$	12.48	1.32
$C_{11}H_8N_2O_2$	12.86	1.16
$C_{11}H_{10}N_2O$	13.23	1.01
$C_{11}H_{12}N_4$	13.60	0.86
$C_{11}H_{20}O_3$	12.32	1.30
$C_{11}H_{22}NO_2$	12.70	1.14
$C_{11}H_{24}N_2O$	13.07	0.99
$C_{11}H_{26}N_2$	13.45	0.84
$C_{12}F_4O_3$	13.21	1.40
$C_{12}H_{10}NO_2$	13.59	1.25
$C_{12}H_{12}N_2O$	13.96	1.10
$C_{12}H_{14}N_2$	13.34	0.96
$C_{12}H_{24}O_2$	13.43	1.23
$C_{12}H_{26}NO$	13.80	1.08
$C_{12}H_{28}N_2$	14.18	0.93
$C_{13}H_2N_3$	15.22	1.08
$C_{13}H_{12}O_2$	14.32	1.35
$C_{13}H_{14}NO$	14.69	1.20
$C_{13}H_{16}N_2$	15.07	1.06
$C_{13}H_{28}O$	14.54	1.18
$C_{14}H_2NO$	15.58	1.33
$C_{14}H_4N_2$	15.96	1.19
$C_{14}H_{16}O$	15.42	1.31
$C_{14}H_{18}N$	15.80	1.17
$C_{15}H_4O$	16.31	1.44
$C_{15}H_6N$	16.69	1.30
$C_{15}H_{20}$	16.53	1.28
$C_{16}H_8$	17.42	1.42
201		
$C_8H_{13}N_2O_4$	9.77	1.23
$C_8H_{15}N_3O_3$	10.15	1.07
$C_8H_{17}N_4O_2$	10.52	0.90
$C_8HN_2O_4$	10.66	1.32
$C_8H_3N_3O_3$	11.04	1.16
$C_8H_5N_4O_2$	11.41	1.00
$C_8H_{15}NO_4$	10.50	1.30
$C_8H_{17}N_2O_3$	10.88	1.14
$C_8H_{19}N_3O_2$	11.25	0.98
$C_8H_{21}N_4O$	11.63	0.82
$C_9H_9NO_4$	11.39	1.39
$C_9H_{11}N_2O_3$	11.77	1.23
$C_9H_{13}N_3O_2$	12.14	1.08
$C_9H_{15}N_4O$	12.52	0.92
$C_9H_{17}O_4$	11.23	1.37
$C_9H_{19}NO_3$	11.61	1.22
$C_9H_{21}N_2O_2$	11.98	1.06
$C_9H_{23}N_3O$	12.36	0.90
$C_9H_{25}N_4$	12.73	0.75
$C_{11}H_5O_4$	12.12	1.47
$C_{11}H_7NO_3$	12.50	1.32
$C_{11}H_9N_2O_2$	12.87	1.16
$C_{11}H_{11}NO$	13.25	1.01
$C_{11}H_{13}N_4$	13.62	0.86
$C_{11}H_{21}O_3$	12.34	1.30
$C_{11}H_{23}NO_2$	12.71	1.14
$C_{11}H_{25}N_2O$	13.09	0.99
$C_{11}H_{27}N_3$	13.46	0.84
$C_{12}HN_4$	14.51	0.98
$C_{12}H_9O_3$	13.23	1.41
$C_{12}H_{11}NO_2$	13.60	1.26
$C_{12}H_{13}N_2O$	13.98	1.11
$C_{12}H_{15}N_3$	14.35	0.96
$C_{12}F_{23}O_2$	13.45	1.23
$C_{12}H_{27}NO$	13.82	1.08
$C_{13}HN_2O$	14.87	1.23
$C_{13}H_3N_3$	15.24	1.08
$C_{13}H_{13}O_2$	14.33	1.35
$C_{13}H_{15}NO$	14.71	1.21
$C_{13}H_{17}N_2$	15.08	1.06
$C_{14}HO_2$	15.22	1.48
$C_{14}H_3NO$	15.60	1.33
$C_{14}H_5N_2$	15.97	1.19
$C_{14}H_{17}O$	15.44	1.31
$C_{14}H_{19}N$	15.81	1.17
$C_{15}H_5O$	16.33	1.45
$C_{15}H_7N$	16.70	1.31
$C_{15}H_{21}$	16.55	1.28
$C_{16}H_9$	17.43	1.43
202		
$C_8H_{14}N_2O_4$	9.79	1.23
$C_8H_{16}N_3O_3$	10.16	1.07
$C_8H_{18}N_4O_2$	10.54	0.91
$C_8H_2N_4O_2$	10.68	1.32
$C_8H_4N_3O_3$	11.05	1.16
$C_8H_6N_4O_2$	11.43	1.00
$C_8H_{16}NO_4$	10.52	1.30
$C_8H_{18}N_2O_3$	10.89	1.14
$C_8H_{20}N_3O_2$	11.27	0.98
$C_8H_{22}N_4O$	11.64	0.82
$C_9H_4NO_4$	11.41	1.39
$C_9H_6N_2O_3$	11.78	1.24
$C_9H_8N_3O_2$	12.16	1.08
$C_9H_{10}N_4O$	12.53	0.92
$C_9H_{12}O_4$	11.25	1.38
$C_9H_{14}NO_3$	11.63	1.22
$C_9H_{16}N_2O_2$	12.00	1.06
$C_9H_{18}N_3O$	12.37	0.91
$C_9H_{20}N_4$	12.75	0.75
$C_{11}H_6O_4$	12.14	1.47
$C_{11}H_8NO_3$	12.51	1.32
$C_{11}H_{10}N_2O_2$	12.89	1.17
$C_{11}H_{12}N_3O$	13.26	1.01
$C_{11}H_{14}N_4$	13.64	0.86
$C_{11}H_{22}O_3$	12.36	1.30
$C_{11}H_{24}NO_2$	12.73	1.15
$C_{11}H_{26}N_2O$	13.11	0.99
$C_{11}H_{28}N_3$	14.53	0.98
$C_{12}H_{12}O_3$	13.25	1.41
$C_{12}H_{14}NO_2$	13.62	1.26
$C_{12}H_{16}N_2O$	13.99	1.11
$C_{12}H_{18}N_3$	14.37	0.96
$C_{12}F_{26}O_2$	13.46	1.24
$C_{12}H_{28}NO$	14.88	1.23
$C_{13}H_4N_3$	15.26	1.09
$C_{13}H_{14}O_2$	14.35	1.35
$C_{13}H_{16}NO$	14.72	1.21
$C_{13}H_{18}N_2$	15.10	1.06
$C_{14}H_2O_2$	15.24	1.48
$C_{14}H_4NO$	15.61	1.34
$C_{14}H_6N_2$	15.99	1.19
$C_{14}H_{18}O$	15.46	1.31
$C_{14}H_{20}N$	15.83	1.17
$C_{15}H_8O$	16.34	1.45
$C_{15}H_8N$	16.72	1.31
$C_{15}H_{22}$	16.56	1.28
$C_{16}H_{10}$	17.45	1.43
203		
$C_8H_{15}N_2O_4$	9.80	1.23
$C_8H_{17}N_3O_3$	10.18	1.07
$C_8H_{19}N_4O_2$	10.55	0.91
$C_8H_3N_2O_4$	10.69	1.32
$C_8H_5N_3O_3$	11.07	1.16
$C_8H_7N_4O_2$	11.44	1.00
$C_8H_{17}NO_4$	10.54	1.30
$C_8H_{19}N_2O_3$	10.91	1.14
$C_8H_{21}N_3O_2$	11.28	0.98
$C_8H_{23}N_4O$	11.66	0.82
$C_{10}H_3NO_4$	11.42	1.40
$C_{10}H_7N_2O_3$	11.80	1.24
$C_{10}H_9N_3O_2$	12.17	1.08
$C_{10}H_{11}N_4O$	12.55	0.93
$C_{10}H_{19}O_4$	11.27	1.38
$C_{10}H_{21}NO_3$	11.64	1.22
$C_{10}H_{23}N_2O_2$	12.02	1.06
$C_{10}H_{25}N_3O$	12.39	0.91
$C_{11}H_7O_4$	12.16	1.48
$C_{11}H_9NO_3$	12.53	1.32
$C_{11}H_{11}N_2O_2$	12.90	1.17
$C_{11}H_{13}N_3O$	13.28	1.02
$C_{11}H_{15}N_4$	13.65	0.86
$C_{11}H_{23}O_3$	12.37	1.30
$C_{11}H_{25}NO_2$	12.75	1.15
$C_{12}HN_3O$	14.17	1.13
$C_{12}H_3N_4$	14.54	0.98
$C_{12}H_{11}O_3$	13.26	1.41
$C_{12}H_{13}NO_2$	13.64	1.26
$C_{12}H_{15}N_2O$	14.01	1.11
$C_{12}H_{17}N_3$	14.38	0.96
$C_{13}HNO_2$	14.52	1.38
$C_{13}H_3N_2O$	14.90	1.23
$C_{13}H_5N_3$	15.27	1.09
$C_{13}H_{15}O_2$	14.37	1.36
$C_{13}H_{17}NO$	14.74	1.21
$C_{13}H_{19}N_2$	15.12	1.06
$C_{14}H_3O_2$	15.26	1.48
$C_{14}H_5NO$	15.63	1.34
$C_{14}H_7N_2$	16.00	1.20
$C_{14}H_{19}O$	15.47	1.32
$C_{14}H_{21}N$	15.85	1.17
$C_{15}H_9O$	16.36	1.45
$C_{15}H_9N$	16.73	1.31
$C_{15}H_{23}$	16.58	1.29
$C_{16}H_{11}$	17.47	1.43
204		
$C_8H_{16}N_2O_4$	9.82	1.24
$C_8H_{18}N_3O_3$	10.19	1.07
$C_8H_{20}N_4O_2$	10.57	0.91
$C_9H_4N_2O_4$	10.71	1.32

	P + 1	P + 2
$C_9H_8N_2O_3$	11.08	1.16
$C_9H_8N_4O_2$	11.46	1.00
$C_9H_{18}NO_4$	10.55	1.31
$C_9H_{26}N_2O_3$	10.93	1.14
$C_9H_{22}N_2O_2$	11.30	0.98
$C_9H_{24}N_4O$	11.67	0.83
$C_{10}H_{12}NO_4$	11.44	1.40
$C_{10}H_{14}N_2O_3$	11.81	1.24
$C_{10}H_{16}N_2O_2$	12.19	1.08
$C_{10}H_{32}N_4O$	12.56	0.93
$C_{10}H_{20}O_4$	11.28	1.38
$C_{10}H_{22}NO_3$	11.66	1.22
$C_{10}H_{24}N_2O_2$	12.03	1.06
$C_{11}H_8O_4$	12.17	1.48
$C_{11}H_{10}NO_3$	12.55	1.32
$C_{11}H_{12}N_2O_2$	12.92	1.17
$C_{11}H_{14}N_3O$	13.29	1.02
$C_{11}H_{16}N_4$	13.67	0.87
$C_{11}H_{24}O_2$	12.39	1.30
$C_{12}H_2N_2O$	14.18	1.13
$C_{12}H_4N_4$	14.56	0.99
$C_{12}H_{12}O_3$	13.28	1.41
$C_{12}H_{14}NO_2$	13.65	1.26
$C_{12}H_{16}N_2O$	14.03	1.11
$C_{12}H_{18}N_3$	14.40	0.96
$C_{13}H_2NO_2$	14.54	1.38
$C_{13}H_4N_2O$	14.91	1.24
$C_{13}H_6N_3$	15.29	1.09
$C_{13}H_{18}O_2$	14.38	1.36
$C_{13}H_{18}NO$	14.76	1.21
$C_{13}H_{20}N_2$	15.13	1.07
$C_{14}H_6O_2$	15.27	1.49
$C_{14}H_8NO$	15.65	1.34
$C_{14}H_{10}N_2$	16.02	1.20
$C_{14}H_{20}O$	15.49	1.32
$C_{14}H_{22}N$	15.86	1.18
$C_{15}H_8O$	16.38	1.45
$C_{15}H_{16}N$	16.75	1.31
$C_{15}H_{24}$	16.59	1.29
$C_{16}H_{12}$	17.48	1.43

205

$C_9H_{17}N_2O_4$	9.84	1.24
$C_9H_{19}N_2O_3$	10.21	1.07
$C_9H_{21}N_4O_2$	10.59	0.91
$C_9H_{13}N_4O_4$	10.73	1.32
$C_9H_{15}N_2O_3$	11.10	1.16
$C_9H_{33}N_4O_2$	11.47	1.00
$C_9H_{33}NO_4$	10.57	1.31
$C_9H_{21}N_2O_3$	10.94	1.15
$C_9H_{23}N_2O_2$	11.32	0.99
$C_{10}H_7NO_4$	11.46	1.40
$C_{10}H_9N_2O_3$	11.83	1.24
$C_{10}H_{11}N_2O_2$	12.21	1.09
$C_{10}H_{13}N_4O$	12.58	0.93
$C_{10}H_{21}O_4$	11.30	1.38
$C_{10}H_{23}NO_3$	11.67	1.22
$C_{11}HN_4O$	13.47	1.04
$C_{11}H_9O_4$	12.19	1.48
$C_{11}H_{11}NO_3$	12.56	1.33
$C_{11}H_{13}N_2O_2$	12.94	1.17
$C_{11}H_{15}N_3O$	13.31	1.02
$C_{11}H_{17}N_4$	13.68	0.87
$C_{12}H_5N_2O_2$	13.82	1.29
$C_{12}H_7N_3O$	14.20	1.14
$C_{12}H_9N_4$	14.57	0.99
$C_{12}H_{13}O_3$	13.29	1.41
$C_{12}H_{15}NO_2$	13.67	1.26
$C_{12}H_{17}N_2O$	14.04	1.11
$C_{12}H_{19}N_3$	14.42	0.97
$C_{13}H_9O_2$	14.18	1.53
$C_{13}H_{11}NO_2$	14.56	1.38
$C_{13}H_{13}N_2O$	14.93	1.24
$C_{13}H_{15}N_3$	15.30	1.09
$C_{13}H_{17}O_2$	14.40	1.36
$C_{13}H_{19}NO$	14.77	1.21
$C_{13}H_{21}N_2$	15.15	1.07
$C_{14}H_5O_2$	15.29	1.49
$C_{14}H_7NO$	15.66	1.34
$C_{14}H_9N_2$	16.04	1.20
$C_{14}H_{21}O$	15.50	1.32
$C_{14}H_{23}N$	15.88	1.18
$C_{15}H_9O$	16.39	1.46
$C_{15}H_{11}N$	16.77	1.32
$C_{15}H_{25}$	16.61	1.29
$C_{16}H_{13}$	17.50	1.44
$C_{17}H$	18.39	1.59

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$C_8H_{18}N_2O_4$	9.85	1.24
$C_8H_{20}N_2O_3$	10.23	1.08
$C_8H_{22}N_4O_2$	10.60	0.91
$C_8H_{14}N_2O_4$	10.74	1.32
$C_8H_{16}N_2O_3$	11.12	1.16
$C_8H_{18}N_4O_2$	11.49	1.01
$C_8H_{30}NO_4$	10.58	1.31
$C_8H_{22}N_2O_3$	10.96	1.15
$C_8H_{24}N_2O_2$	11.47	1.40
$C_9H_{10}N_2O_3$	11.85	1.24
$C_9H_{12}N_2O_2$	12.22	1.09
$C_9H_{14}N_4O$	12.60	0.93
$C_9H_{22}O_4$	11.31	1.38
$C_{11}H_2N_4O$	13.48	1.04
$C_{11}H_{10}O_4$	12.20	1.48
$C_{11}H_{12}NO_3$	12.58	1.33
$C_{11}H_{14}N_2O_2$	12.95	1.17
$C_{11}H_{16}N_3O$	13.33	1.02
$C_{11}H_{18}N_4$	13.70	0.87
$C_{12}H_6N_2O_2$	13.84	1.29
$C_{12}H_8N_3O$	14.22	1.14
$C_{12}H_{10}N_4$	14.59	0.99
$C_{12}H_{14}O_3$	13.31	1.42
$C_{12}H_{16}NO_2$	13.68	1.27
$C_{12}H_{18}N_2O$	14.06	1.12
$C_{12}H_{20}N_3$	14.43	0.97
$C_{13}H_8O_2$	14.20	1.53
$C_{13}H_{10}NO_2$	14.57	1.39
$C_{13}H_{12}N_2O$	14.95	1.24
$C_{13}H_{14}N_3$	15.32	1.10
$C_{13}H_{16}O_2$	14.41	1.36
$C_{13}H_{26}NO$	14.79	1.22
$C_{13}H_{22}N_2$	15.16	1.07
$C_{14}H_8O_2$	15.30	1.49
$C_{14}H_{10}NO$	15.68	1.35
$C_{14}H_{12}N_2$	16.05	1.21
$C_{14}H_{22}O$	15.52	1.32
$C_{14}H_{24}N$	15.89	1.18
$C_{15}H_{10}O$	16.41	1.46
$C_{15}H_{12}N$	16.78	1.32
$C_{15}H_{26}$	16.63	1.29
$C_{16}H_{14}$	17.51	1.44
$C_{17}H_2$	18.40	1.59

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$C_8H_{18}N_2O_4$	9.87	1.24
$C_8H_{17}NO_5$	10.24	1.08
$C_8H_{17}NO_4$	10.76	1.33
$C_8H_{19}N_2O_3$	11.13	1.17
$C_8H_{11}N_4O_2$	11.51	1.01
$C_8H_{21}NO_4$	10.60	1.31
$C_{10}H_8NO_4$	11.49	1.40
$C_{10}H_{11}N_2O_3$	11.86	1.25
$C_{10}H_{13}N_2O_2$	12.24	1.09
$C_{11}H_{13}N_4O$	12.61	0.93
$C_{11}H_{15}NO_3$	13.13	1.20
$C_{11}H_{17}N_2O$	13.50	1.04
$C_{11}H_{11}O_4$	12.22	1.48
$C_{11}H_{13}NO_3$	12.59	1.33
$C_{11}H_{15}N_2O_2$	12.97	1.18
$C_{11}H_{17}N_3O$	13.34	1.02
$C_{11}H_{19}N_4$	13.72	0.87
$C_{12}HNO_3$	13.48	1.44
$C_{12}H_3N_2O_2$	13.86	1.29
$C_{12}H_5N_3O$	14.23	1.14
$C_{12}H_7N_4$	14.61	0.99
$C_{12}H_{15}O_3$	13.33	1.42
$C_{12}H_{17}NO_2$	13.70	1.27
$C_{12}H_{19}N_2O$	14.07	1.12
$C_{12}H_{21}N_3$	14.45	0.97
$C_{13}H_9O_2$	14.21	1.54
$C_{13}H_{11}NO_2$	14.59	1.39
$C_{13}H_{13}N_2O$	14.96	1.24
$C_{13}H_{15}N_3$	15.34	1.10
$C_{13}H_{17}O_2$	14.43	1.37
$C_{13}H_{21}NO$	14.80	1.22
$C_{13}H_{23}N_2$	15.18	1.07
$C_{14}H_7O_2$	15.32	1.49
$C_{14}H_9NO$	15.69	1.35
$C_{14}H_{11}N_2$	16.07	1.21
$C_{14}H_{23}O$	15.54	1.33
$C_{14}H_{23}N$	15.91	1.18
$C_{15}H_{11}O$	16.42	1.46
$C_{15}H_{13}N$	16.80	1.32
$C_{15}H_{27}$	16.64	1.30
$C_{16}HN$	17.69	1.47
$C_{16}H_{15}$	17.53	1.44
$C_{17}H_3$	18.42	1.60

208

$C_8H_{16}N_2O_4$	9.88	1.24
$C_8H_{18}N_2O_4$	10.77	1.33
$C_8H_{16}N_2O_3$	11.15	1.17
$C_8H_{12}N_4O_2$	11.52	1.01
$C_8H_{14}NO_4$	11.50	1.40
$C_{10}H_{12}N_2O_3$	11.88	1.25
$C_{10}H_{14}N_2O_2$	12.25	1.09
$C_{10}H_{16}N_4O$	12.63	0.94
$C_{11}H_{12}N_2O_2$	13.14	1.20
$C_{11}H_4N_4O$	13.52	1.05
$C_{11}H_{12}O_4$	12.24	1.49
$C_{11}H_{14}NO_3$	12.61	1.33
$C_{11}H_{16}N_2O_2$	12.98	1.18
$C_{11}H_{18}N_3O$	13.36	1.03
$C_{11}H_{20}N_4$	13.73	0.88
$C_{12}H_8NO_3$	13.50	1.44
$C_{12}H_{10}N_2O_2$	13.87	1.29
$C_{12}H_{12}N_3O$	14.25	1.14
$C_{12}H_{14}N_4$	14.62	1.00
$C_{12}H_{16}O_3$	13.34	1.42
$C_{12}H_{18}NO_2$	13.72	1.27
$C_{12}H_{20}N_2O$	14.09	1.12
$C_{12}H_{22}N_3$	14.46	0.97
$C_{13}H_6O_2$	14.23	1.54
$C_{13}H_8NO_2$	14.60	1.39
$C_{13}H_{10}N_2O$	14.98	1.24
$C_{13}H_{12}N_3$	15.35	1.10
$C_{13}H_{26}O_2$	14.45	1.37
$C_{13}H_{22}NO$	14.82	1.22
$C_{13}H_{24}N_2$	15.20	1.08
$C_{14}H_8O_2$	15.34	1.50
$C_{14}H_{10}NO$	15.71	1.35
$C_{14}H_{12}N_2$	16.08	1.21
$C_{14}H_{24}O$	15.55	1.33
$C_{14}H_{26}N$	15.93	1.19
$C_{15}H_{12}O$	16.44	1.46
$C_{15}H_{14}N$	16.81	1.33
$C_{15}H_{28}$	16.66	1.30
$C_{16}H_2N$	17.70	1.47
$C_{16}H_{16}$	17.55	1.45
$C_{17}H_4$	18.43	1.60

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$C_9H_9N_2O_4$	10.79	1.33
$C_9H_{11}N_2O_3$	11.16	1.17
$C_9H_{13}N_4O_2$	11.54	1.01
$C_{10}HN_4O_2$	12.43	1.11
$C_{10}H_{11}NO_4$	11.52	1.41
$C_{10}H_{13}N_2O_3$	11.89	1.25
$C_{10}H_{15}N_2O_2$	12.27	1.09
$C_{10}H_{17}N_4O$	12.64	0.94
$C_{11}H_7N_2O_3$	12.78	1.35
$C_{11}H_9N_2O_2$	13.16	1.20
$C_{11}H_{11}N_4O$	13.53	1.05
$C_{11}H_{13}O_4$	12.25	1.49
$C_{11}H_{15}NO_3$	12.63	1.33
$C_{11}H_{17}N_2O_2$	13.00	1.18
$C_{11}H_{19}N_3O$	13.37	1.03
$C_{11}H_{21}N_4$	13.75	0.88
$C_{12}HO_4$	13.14	1.60
$C_{12}H_3NO_3$	13.51	1.44
$C_{12}H_5N_2O_2$	13.89	1.29
$C_{12}H_7N_3O$	14.26	1.15
$C_{12}H_9N_4$	14.64	1.00
$C_{12}H_{17}O_3$	13.36	1.42
$C_{12}H_{19}NO_2$	13.73	1.27
$C_{12}H_{21}N_2O$	14.11	1.12
$C_{12}H_{23}N_3$	14.48	0.98
$C_{13}H_9O_2$	14.25	1.54
$C_{13}H_{11}NO_2$	14.62	1.39
$C_{13}H_{13}N_2O$	14.99	1.25
$C_{13}H_{15}N_3$	15.37	1.10

	P + 1	P + 2
$C_{13}H_{21}O_2$	14.46	1.37
$C_{13}H_{23}NO$	14.84	1.22
$C_{13}H_{25}N_2$	15.21	1.08
$C_{14}H_9O_2$	15.35	1.50
$C_{14}H_{11}NO$	15.73	1.35
$C_{14}H_{13}N_2$	16.10	1.21
$C_{14}H_{25}O$	15.57	1.33
$C_{14}H_{27}N$	15.94	1.19
$C_{15}H_9N_2$	16.99	1.35
$C_{15}H_{13}O$	16.46	1.47
$C_{15}H_{15}N$	16.83	1.33
$C_{15}H_{29}$	16.67	1.30
$C_{16}HO$	17.35	1.61
$C_{16}H_9N$	17.72	1.48
$C_{16}H_{17}$	17.56	1.45
$C_{17}H_5$	18.45	1.60
210		
$C_9H_{16}N_2O_4$	10.81	1.33
$C_9H_{12}N_2O_3$	11.18	1.17
$C_9H_{14}N_4O_2$	11.55	1.01
$C_{10}H_{12}N_4O_2$	12.44	1.11
$C_{10}H_{12}NO_4$	11.54	1.41
$C_{10}H_{14}N_2O_3$	11.91	1.25
$C_{10}H_{16}N_4O_2$	12.29	1.09
$C_{10}H_{18}N_4O$	12.66	0.94
$C_{11}H_8N_2O_3$	12.80	1.35
$C_{11}H_{14}N_2O_3$	13.17	1.20
$C_{11}H_6N_4O$	13.55	1.05
$C_{11}H_{14}O_4$	12.27	1.49
$C_{11}H_{16}NO_3$	12.64	1.34
$C_{11}H_{18}N_2O_2$	13.02	1.18
$C_{11}H_{26}N_2O$	13.39	1.03
$C_{11}H_{22}N_4$	13.76	0.88
$C_{12}H_8O_4$	13.16	1.60
$C_{12}H_4NO_3$	13.53	1.45
$C_{12}H_6N_2O_2$	13.90	1.30
$C_{12}H_8N_2O$	14.28	1.15
$C_{12}H_{16}N_4$	14.65	1.00
$C_{12}H_{18}O_3$	13.37	1.43
$C_{12}H_{26}NO_2$	13.75	1.28
$C_{12}H_{22}N_2O$	14.12	1.13
$C_{12}H_{24}N_2$	14.50	0.98
$C_{13}H_6O_3$	14.26	1.54
$C_{13}H_8NO_2$	14.64	1.40
$C_{13}H_{16}N_2O$	15.01	1.25
$C_{13}H_{12}N_3$	15.38	1.11
$C_{13}H_{22}O_2$	14.48	1.37
$C_{13}H_{24}NO$	14.85	1.23
$C_{13}H_{26}N_2$	15.23	1.08
$C_{14}H_{16}O_2$	15.37	1.50
$C_{14}H_{18}NO$	15.74	1.36
$C_{14}H_{14}N_2$	16.12	1.22
$C_{14}H_{26}O$	15.58	1.33
$C_{14}H_{28}N$	15.96	1.19
$C_{15}H_2N_2$	17.00	1.36
$C_{15}H_{14}O$	16.47	1.47
$C_{15}H_{16}N$	16.85	1.33
$C_{15}H_{30}$	16.69	1.31
$C_{16}H_8O$	17.36	1.61
$C_{16}H_4N$	17.74	1.48
$C_{16}H_{18}$	17.58	1.45
$C_{17}H_6$	18.47	1.61
211		
$C_9H_{11}N_2O_4$	10.82	1.33
$C_9H_{13}N_2O_3$	11.20	1.17
$C_9H_{15}N_4O_2$	11.57	1.01
$C_{10}H_{13}N_2O_3$	12.08	1.27
$C_{10}H_{15}N_4O_2$	12.46	1.12
$C_{10}H_{17}N_4O_2$	11.55	1.41
$C_{10}H_{15}N_2O_3$	11.93	1.25
$C_{10}H_{17}N_2O_2$	12.30	1.10
$C_{10}H_{19}N_4O$	12.68	0.94
$C_{11}HNO_4$	12.44	1.51
$C_{11}H_3N_2O_3$	12.82	1.36
$C_{11}H_5N_2O_2$	13.19	1.20
$C_{11}H_7N_4O$	13.56	1.05
$C_{11}H_{15}O_4$	12.28	1.49
$C_{11}H_{17}NO_3$	12.66	1.34
$C_{11}H_{19}N_2O_2$	13.03	1.18
$C_{11}H_{21}N_2O$	13.41	1.03
$C_{11}H_{23}N_4$	13.78	0.88
$C_{12}H_9O_4$	13.17	1.60
$C_{12}H_5NO_3$	13.55	1.45
$C_{12}H_7N_2O_2$	13.92	1.30
$C_{12}H_9N_2O$	14.30	1.15
$C_{12}H_{11}N_4$	14.67	1.60
$C_{12}H_{13}O_3$	13.39	1.43
$C_{12}H_{21}NO_2$	13.76	1.28
$C_{12}H_{23}N_2O$	14.14	1.13
$C_{12}H_{25}N_3$	14.51	0.98
$C_{13}H_{17}O_3$	14.28	1.54
$C_{13}H_{19}NO_2$	14.65	1.40
$C_{13}H_{11}N_2O$	15.03	1.25
$C_{13}H_{13}N_3$	15.40	1.11
$C_{13}H_{23}O_2$	14.49	1.38
$C_{13}H_{25}NO$	14.87	1.23
$C_{13}H_{27}N_2$	15.24	1.08
$C_{14}HN_3$	16.29	1.24
$C_{14}H_{11}O_3$	15.38	1.50
$C_{14}H_{13}NO$	15.76	1.36
$C_{14}H_{15}N_2$	16.13	1.22
$C_{14}H_{27}O$	15.60	1.34
$C_{14}H_{29}N$	15.97	1.19
$C_{15}HNO$	16.65	1.50
$C_{15}H_3N_2$	17.02	1.36
$C_{15}H_{15}O$	16.49	1.47
$C_{15}H_{17}N$	16.86	1.33
$C_{15}H_{31}$	16.71	1.31
$C_{16}H_9O$	17.38	1.62
$C_{16}H_{11}N$	17.75	1.48
$C_{16}H_{33}$	17.59	1.45
$C_{17}H_7$	18.48	1.61
212		
$C_8H_{16}N_2O_4$	10.84	1.34
$C_8H_{14}N_2O_3$	11.21	1.18
$C_8H_{16}N_4O_2$	11.59	1.02
$C_{10}H_{14}N_2O_3$	12.10	1.27
$C_{10}H_{16}N_4O_2$	12.47	1.12
$C_{10}H_{14}NO_4$	11.57	1.41
$C_{10}H_{16}N_2O_3$	11.94	1.25
$C_{10}H_{18}N_2O_2$	12.32	1.10
$C_{10}H_{20}N_4O$	12.69	0.94
$C_{11}H_2NO_4$	12.46	1.51
$C_{11}H_4N_2O_3$	12.83	1.36
$C_{11}H_6N_2O_2$	13.21	1.21
$C_{11}H_8N_4O$	13.58	1.06
$C_{11}H_{16}O_4$	12.30	1.49
$C_{11}H_{18}NO_3$	12.67	1.34
$C_{11}H_{20}N_2O_2$	13.05	1.19
$C_{11}H_{22}N_2O$	13.42	1.03
$C_{11}H_{24}N_4$	13.80	0.88
$C_{12}H_4O_4$	13.19	1.60
$C_{12}H_6NO_3$	13.56	1.45
$C_{12}H_8N_2O_2$	13.94	1.30
$C_{12}H_{10}N_2O$	14.31	1.15
$C_{12}H_{12}N_4$	14.69	1.01
$C_{12}H_{20}O_3$	13.41	1.43
$C_{12}H_{22}NO_2$	13.78	1.28
$C_{12}H_{24}N_2O$	14.15	1.13
$C_{12}H_{26}N_3$	14.53	0.98
$C_{13}H_8O_3$	14.29	1.55
$C_{13}H_{10}NO_2$	14.67	1.40
$C_{13}H_{12}N_2O$	15.04	1.25
$C_{13}H_{14}N_3$	15.42	1.11
$C_{13}H_{24}O_2$	14.51	1.38
$C_{13}H_{26}NO$	14.88	1.23
$C_{13}H_{28}N_2$	15.26	1.09
$C_{14}H_2N_3$	16.31	1.25
$C_{14}H_{12}O_2$	15.40	1.50
$C_{14}H_{14}NO$	15.77	1.36
$C_{14}H_{16}N_2$	16.15	1.22
$C_{14}H_{28}O$	15.62	1.34
$C_{14}H_{30}N$	15.99	1.20
$C_{15}H_2NO$	16.66	1.50
$C_{15}H_4N_2$	17.04	1.36
$C_{15}H_{16}O$	16.50	1.47
$C_{15}H_{18}N$	16.88	1.34
$C_{15}H_{32}$	16.72	1.31
$C_{16}H_{10}O$	17.39	1.62
$C_{16}H_{12}N$	17.77	1.48
$C_{16}H_{20}$	17.61	1.46
$C_{17}H_8$	18.50	1.61
213		
$C_8H_9N_2O_4$	10.86	1.34
$C_8H_{15}N_2O_3$	11.23	1.18
$C_8H_{17}N_4O_2$	11.60	1.02
$C_{10}H_{15}N_2O_3$	11.74	1.43
$C_{10}H_{17}N_2O_2$	12.12	1.27
$C_{10}H_{19}N_4O_2$	12.49	1.12
$C_{10}H_{15}NO_4$	11.58	1.41
$C_{10}H_{17}N_2O_3$	11.96	1.26
$C_{10}H_{19}N_2O_2$	12.33	1.10
$C_{10}H_{21}N_4O$	12.71	0.95
$C_{11}H_3NO_4$	12.47	1.51
$C_{11}H_5N_2O_3$	12.85	1.36
$C_{11}H_7N_2O_2$	13.22	1.21
$C_{11}H_9N_4O$	13.60	1.06
$C_{11}H_{17}O_4$	12.32	1.50
$C_{11}H_{19}NO_3$	12.69	1.34
$C_{11}H_{21}N_2O_2$	13.06	1.19
$C_{11}H_{23}N_2O$	13.44	1.04
$C_{11}H_{25}N_4$	13.81	0.89
$C_{12}H_5O_4$	13.20	1.60
$C_{12}H_7NO_3$	13.58	1.45
$C_{12}H_9N_2O_2$	13.95	1.30
$C_{12}H_{11}N_2O$	14.33	1.15
$C_{12}H_{13}N_4$	14.70	1.01
$C_{12}H_{21}O_3$	13.42	1.43
$C_{12}H_{23}NO_2$	13.80	1.28
$C_{12}H_{25}N_2O$	14.17	1.13
$C_{12}H_{27}N_3$	14.54	0.99
$C_{13}HN_4$	15.59	1.14
$C_{13}H_9O_3$	14.31	1.55
$C_{13}H_{11}NO_2$	14.68	1.40
$C_{13}H_{13}N_2O$	15.06	1.26
$C_{13}H_{15}N_3$	15.43	1.11
$C_{13}H_{25}O_2$	14.53	1.38
$C_{13}H_{27}NO$	14.90	1.23
$C_{13}H_{29}N_2$	15.28	1.09
$C_{14}HN_2O$	15.95	1.39
$C_{14}HN_3$	16.32	1.25
$C_{14}H_{13}O_2$	15.42	1.51
$C_{14}H_{15}NO$	15.79	1.36
$C_{14}H_{17}N_2$	16.16	1.22
$C_{14}H_{29}O$	15.63	1.34
$C_{14}H_{31}N$	16.01	1.20
$C_{15}HO_2$	16.30	1.64
$C_{15}H_3NO$	16.68	1.50
$C_{15}H_5N_2$	17.05	1.36
$C_{15}H_{17}O$	16.52	1.48
$C_{15}H_{19}N$	16.90	1.34
$C_{16}H_5O$	17.41	1.62
$C_{16}H_7N$	17.78	1.49
$C_{16}H_{21}$	17.63	1.46
$C_{17}H_9$	18.51	1.61
214		
$C_8H_{14}N_2O_4$	10.87	1.34
$C_8H_{12}N_2O_3$	11.24	1.18
$C_8H_{14}N_4O_2$	11.62	1.02
$C_{10}H_{12}N_2O_3$	11.76	1.43
$C_{10}H_{14}N_2O_3$	12.13	1.28
$C_{10}H_{16}N_4O_2$	12.51	1.12
$C_{10}H_{18}NO_4$	11.60	1.42
$C_{10}H_{16}N_2O_3$	11.97	1.26
$C_{10}H_{20}N_2O_2$	12.35	1.10
$C_{10}H_{22}N_4O$	12.72	0.95
$C_{11}H_4NO_4$	12.49	1.52
$C_{11}H_6N_2O_3$	12.86	1.36
$C_{11}H_8N_2O_2$	13.24	1.21
$C_{11}H_{10}N_4O$	13.61	1.06
$C_{11}H_{18}O_4$	12.33	1.50
$C_{11}H_{20}NO_3$	12.71	1.34
$C_{11}H_{22}N_2O_2$	13.08	1.19
$C_{11}H_{24}N_2O$	13.45	1.04
$C_{11}H_{26}N_4$	13.83	0.89
$C_{12}H_6O_4$	13.22	1.61
$C_{12}H_8NO_3$	13.59	1.45
$C_{12}H_{10}N_2O_2$	13.97	1.31
$C_{12}H_{12}N_2O$	14.34	1.16
$C_{12}H_{14}N_4$	14.72	1.01
$C_{12}H_{22}O_3$	13.44	1.43
$C_{12}H_{24}NO_2$	13.81	1.28
$C_{12}H_{26}N_2O$	14.19	1.14
$C_{12}H_{28}N_3$	14.56	0.99
$C_{13}H_2N_4$	15.61	1.14
$C_{13}H_{10}O_3$	14.33	1.55
$C_{13}H_{12}NO_2$	14.70	1.40
$C_{13}H_{14}N_2O$	15.07	1.26

	P + 1	P + 2
$C_{13}H_{16}N_3$	15.45	1.12
$C_{13}H_{26}O_2$	14.54	1.38
$C_{13}H_{29}NO$	14.92	1.24
$C_{13}H_{30}N_2$	15.29	1.09
$C_{14}H_2N_2O$	15.96	1.39
$C_{14}H_4N_2$	16.34	1.25
$C_{14}H_4O_2$	15.43	1.51
$C_{14}H_{18}NO$	15.81	1.37
$C_{14}H_{19}N_2$	16.18	1.23
$C_{14}H_{30}O$	15.65	1.34
$C_{15}H_2O_2$	16.32	1.64
$C_{15}H_4NO$	16.69	1.51
$C_{15}H_5N_2$	17.07	1.37
$C_{15}H_{19}O$	16.54	1.48
$C_{15}H_{20}N$	16.91	1.34
$C_{16}H_8O$	17.43	1.63
$C_{16}H_8N$	17.80	1.49
$C_{16}H_{22}$	17.64	1.46
$C_{17}H_{10}$	18.53	1.62
215		
$C_9H_{15}N_2O_4$	10.89	1.34
$C_9H_{17}N_2O_3$	11.26	1.18
$C_9H_{19}N_4O_2$	11.63	1.02
$C_{10}H_5N_2O_4$	11.77	1.44
$C_{10}H_5N_2O_3$	12.15	1.28
$C_{10}H_7N_4O_2$	12.52	1.12
$C_{10}H_{17}NO_4$	11.62	1.42
$C_{10}H_{18}N_2O_3$	11.99	1.26
$C_{10}H_{21}N_2O_2$	12.37	1.10
$C_{10}H_{22}N_4O$	12.74	0.95
$C_{11}H_5NO_4$	12.50	1.52
$C_{11}H_7N_2O_3$	12.88	1.37
$C_{11}H_9N_3O_2$	13.25	1.21
$C_{11}H_{11}N_4O$	13.63	1.06
$C_{11}H_{19}O_4$	12.35	1.50
$C_{11}H_{21}NO_3$	12.72	1.35
$C_{11}H_{23}N_2O_2$	13.10	1.19
$C_{11}H_{25}N_3O$	13.47	1.04
$C_{11}H_{27}N_4$	13.84	0.89
$C_{12}H_7O_4$	13.24	1.61
$C_{12}H_9NO_3$	13.61	1.46
$C_{12}H_{11}N_2O_2$	13.98	1.31
$C_{12}H_{13}N_3O$	14.36	1.16
$C_{12}H_{15}N_4$	14.73	1.01
$C_{12}H_{23}O_3$	13.45	1.44
$C_{12}H_{25}NO_2$	13.83	1.29
$C_{12}H_{27}N_2O$	14.20	1.14
$C_{12}H_{29}N_3$	14.58	0.99
$C_{13}HN_3O$	15.25	1.28
$C_{13}H_3N_4$	15.62	1.14
$C_{13}H_{11}O_3$	14.34	1.55
$C_{13}H_{13}NO_2$	14.72	1.41
$C_{13}H_{15}N_2O$	15.09	1.26
$C_{13}H_{17}N_3$	15.46	1.12
$C_{13}H_{27}O_2$	14.56	1.38
$C_{13}H_{29}NO$	14.93	1.24
$C_{14}HNO_2$	15.60	1.54
$C_{14}H_3N_2O$	15.98	1.39
$C_{14}H_5N_3$	16.35	1.25
$C_{14}H_{15}O_2$	15.45	1.51
$C_{14}H_{17}NO$	15.82	1.37
$C_{14}H_{18}N_2$	16.20	1.23
$C_{15}H_3O_2$	16.34	1.65
$C_{15}H_5NO$	16.71	1.51
$C_{15}H_7N_2$	17.08	1.37
$C_{15}H_{19}O$	16.55	1.48
$C_{15}H_{21}N$	16.93	1.34
$C_{16}H_9O$	17.44	1.63
$C_{16}H_9N$	17.82	1.49
$C_{16}H_{23}$	17.66	1.47
$C_{17}H_{11}$	18.55	1.62
216		
$C_8H_{16}N_2O_4$	10.90	1.34
$C_8H_{18}N_3O_3$	11.28	1.18
$C_8H_{20}N_4O_2$	11.65	1.02
$C_{10}H_4N_2O_4$	11.79	1.44
$C_{10}H_6N_2O_3$	12.16	1.28
$C_{10}H_8N_4O_2$	12.54	1.13
$C_{10}H_{18}NO_4$	11.63	1.42
$C_{10}H_{20}N_2O_3$	12.01	1.26
$C_{10}H_{22}N_3O_2$	12.38	1.11
$C_{10}H_{24}N_4O$	12.76	0.95
$C_{11}H_6NO_4$	12.52	1.52
$C_{11}H_8N_2O_3$	12.90	1.37
$C_{11}H_{10}N_3O_2$	13.27	1.21
$C_{11}H_{12}N_4O$	13.64	1.06
$C_{11}H_{20}O_4$	12.36	1.50
$C_{11}H_{22}NO_3$	12.74	1.35
$C_{11}H_{24}N_2O_2$	13.11	1.19
$C_{11}H_{26}N_3O$	13.49	1.04
$C_{11}H_{28}N_4$	13.86	0.89
$C_{12}H_8O_4$	13.25	1.61
$C_{12}H_{10}NO_3$	13.63	1.46
$C_{12}H_{12}N_2O_2$	14.00	1.31
$C_{12}H_{14}N_3O$	14.38	1.16
$C_{12}H_{16}N_4$	14.75	1.01
$C_{12}H_{24}O_3$	13.47	1.44
$C_{12}H_{26}NO_2$	13.84	1.29
$C_{12}H_{28}N_2O$	14.22	1.14
$C_{12}H_{30}N_3$	15.26	1.29
$C_{13}H_4N_4$	15.64	1.14
$C_{13}H_{12}O_3$	14.36	1.56
$C_{13}H_{14}NO_2$	14.73	1.41
$C_{13}H_{16}N_2O$	15.11	1.26
$C_{13}H_{18}N_3$	15.48	1.12
$C_{13}H_{28}O_2$	14.57	1.39
$C_{14}H_2NO_2$	15.62	1.54
$C_{14}H_4N_2O$	15.99	1.40
$C_{14}H_6N_3$	16.37	1.26
$C_{14}H_{16}O_2$	15.46	1.51
$C_{14}H_{18}NO$	15.84	1.37
$C_{14}H_{20}N_2$	16.21	1.23
$C_{15}H_4O_2$	16.35	1.65
$C_{15}H_6NO$	16.73	1.51
$C_{15}H_8N_2$	17.10	1.37
$C_{15}H_{20}O$	16.57	1.49
$C_{15}H_{22}N$	16.94	1.35
$C_{16}H_{10}O$	17.46	1.63
$C_{16}H_{10}N$	17.83	1.50
$C_{16}H_{24}$	17.67	1.47
$C_{17}H_{12}$	18.56	1.62
217		
$C_8H_{17}N_2O_4$	10.92	1.34
$C_8H_{19}N_3O_3$	11.29	1.18
$C_8H_{21}N_4O_2$	11.67	1.03
$C_{10}H_5N_2O_4$	11.81	1.44
$C_{10}H_7N_3O_3$	12.18	1.28
$C_{10}H_9N_4O_2$	12.55	1.13
$C_{10}H_{19}NO_4$	11.65	1.42
$C_{10}H_{21}N_2O_3$	12.02	1.26
$C_{10}H_{23}N_3O_2$	12.40	1.11
$C_{10}H_{25}N_4O$	12.77	0.95
$C_{11}H_7NO_4$	12.54	1.52
$C_{11}H_9N_2O_3$	12.91	1.37
$C_{11}H_{11}N_3O_2$	13.29	1.22
$C_{11}H_{13}N_4O$	13.66	1.07
$C_{11}H_{21}O_4$	12.38	1.50
$C_{11}H_{23}NO_3$	12.75	1.35
$C_{11}H_{25}N_2O_2$	13.13	1.20
$C_{11}H_{27}N_3O$	13.50	1.05
$C_{11}HN_4O$	14.55	1.19
$C_{12}H_9O_4$	13.27	1.61
$C_{12}H_{11}NO_3$	13.64	1.46
$C_{12}H_{13}N_2O_2$	14.02	1.31
$C_{12}H_{15}N_3O$	14.39	1.16
$C_{12}H_{17}N_4$	14.77	1.02
$C_{12}H_{25}O_3$	13.49	1.44
$C_{12}H_{27}NO_2$	13.86	1.29
$C_{12}H_{29}N_2O$	14.91	1.43
$C_{12}H_{31}N_3$	15.28	1.29
$C_{13}H_5N_4$	15.65	1.15
$C_{13}H_{13}O_3$	14.37	1.56
$C_{13}H_{15}NO_2$	14.75	1.41
$C_{13}H_{17}N_2O$	15.12	1.27
$C_{13}H_{19}N_3$	15.50	1.12
$C_{14}HO_3$	15.26	1.68
$C_{14}H_3NO_2$	15.64	1.54
$C_{14}H_5N_2O$	16.01	1.40
$C_{14}H_7N_3$	16.39	1.26
$C_{14}H_{17}O_2$	15.48	1.52
$C_{14}H_{19}NO$	15.58	1.37
$C_{14}H_{21}N_2$	16.23	1.23
$C_{15}H_5O_2$	16.37	1.65
$C_{15}H_7NO$	16.74	1.51
$C_{15}H_9N_2$	17.12	1.38
$C_{15}H_{21}O$	16.58	1.49
$C_{15}H_{23}N$	16.96	1.35
$C_{16}H_{11}O$	17.47	1.63
$C_{16}H_{11}N$	17.85	1.50
$C_{16}H_{25}$	17.69	1.47
$C_{17}H_{13}$	18.58	1.63
$C_{18}H$	19.47	1.79
218		
$C_8H_{18}N_2O_4$	10.93	1.35
$C_8H_{20}N_3O_3$	11.31	1.19
$C_8H_{22}N_4O_2$	11.68	1.03
$C_{10}H_6N_2O_4$	11.82	1.44
$C_{10}H_8N_3O_3$	12.20	1.28
$C_{10}H_{10}N_4O_2$	12.57	1.13
$C_{10}H_{20}NO_4$	11.66	1.42
$C_{10}H_{22}N_2O_3$	12.04	1.27
$C_{10}H_{24}N_3O_2$	12.41	1.11
$C_{10}H_{26}N_4O$	12.79	0.96
$C_{11}H_8NO_4$	12.55	1.52
$C_{11}H_{10}N_2O_3$	12.93	1.37
$C_{11}H_{12}N_3O_2$	13.30	1.22
$C_{11}H_{14}N_4O$	13.68	1.07
$C_{11}H_{22}O_4$	12.40	1.51
$C_{11}H_{24}NO_3$	12.77	1.35
$C_{11}H_{26}N_2O_2$	13.14	1.20
$C_{11}H_{28}N_3O$	14.56	1.19
$C_{12}H_{10}O_4$	13.28	1.61
$C_{12}H_{12}NO_3$	13.66	1.46
$C_{12}H_{14}N_2O_2$	14.03	1.31
$C_{12}H_{16}N_3O$	14.41	1.17
$C_{12}H_{18}N_4$	14.78	1.02
$C_{12}H_{26}O_3$	13.50	1.44
$C_{12}H_{28}N_2O_2$	14.92	1.44
$C_{12}H_{30}N_3O$	15.30	1.29
$C_{13}H_6N_4$	15.67	1.15
$C_{13}H_{14}O_3$	14.39	1.56
$C_{13}H_{16}NO_2$	14.76	1.41
$C_{13}H_{18}N_2O$	15.14	1.27
$C_{13}H_{20}N_3$	15.51	1.13
$C_{14}H_2O_3$	15.28	1.69
$C_{14}H_4NO_2$	15.65	1.54
$C_{14}H_6N_2O$	16.03	1.40
$C_{14}H_8N_3$	16.40	1.26
$C_{14}H_{18}O_2$	15.50	1.52
$C_{14}H_{20}NO$	15.87	1.38
$C_{14}H_{22}N_2$	16.24	1.24
$C_{15}H_6O_2$	16.38	1.66
$C_{15}H_8NO$	16.76	1.52
$C_{15}H_{10}N_2$	17.13	1.38
$C_{15}H_{22}O$	16.60	1.49
$C_{15}H_{24}N$	16.98	1.35
$C_{16}H_{12}O$	17.49	1.64
$C_{16}H_{12}N$	17.86	1.50
$C_{16}H_{26}$	17.71	1.47
$C_{17}H_{14}$	18.59	1.63
$C_{18}H_2$	19.48	1.79
219		
$C_9H_{18}N_2O_4$	10.95	1.35
$C_9H_{21}N_3O_3$	11.32	1.19
$C_9H_{23}N_4O_2$	11.70	1.03
$C_{10}H_7N_2O_4$	11.84	1.44
$C_{10}H_9N_3O_3$	12.21	1.29
$C_{10}H_{11}N_4O_2$	12.59	1.13
$C_{10}H_{21}NO_4$	11.68	1.42
$C_{10}H_{23}N_2O_3$	12.05	1.27
$C_{10}H_{25}N_3O_2$	12.43	1.11
$C_{11}H_9NO_4$	12.57	1.53
$C_{11}H_{11}N_2O_3$	12.94	1.37
$C_{11}H_{13}N_3O_2$	13.32	1.22
$C_{11}H_{15}N_4O$	13.69	1.07
$C_{11}H_{23}O_4$	12.41	1.51
$C_{11}H_{25}NO_3$	12.79	1.35
$C_{11}H_{27}N_2O_2$	13.17	1.20
$C_{11}H_{29}N_3O$	13.54	1.05
$C_{12}H_{11}O_4$	13.30	1.62
$C_{12}H_{13}NO_3$	13.67	1.47
$C_{12}H_{15}N_2O_2$	14.05	1.32
$C_{12}H_{17}N_3O$	14.42	1.17
$C_{12}H_{19}N_4$	14.80	1.02
$C_{13}HNO_3$	14.56	1.59
$C_{13}H_3N_2O_2$	14.94	1.44
$C_{13}H_5N_3O$	15.31	1.29

	P + 1	P + 2
$C_{13}H_{17}N_4$	15.69	1.15
$C_{13}H_{18}O_3$	14.41	1.56
$C_{13}H_{17}NO_2$	14.78	1.42
$C_{13}H_{19}N_2O$	15.15	1.27
$C_{13}H_{21}N_3$	15.53	1.13
$C_{14}H_3O_3$	15.29	1.69
$C_{14}H_5NO_2$	15.67	1.55
$C_{14}H_7N_2O$	16.04	1.40
$C_{14}H_9N_3$	16.42	1.26
$C_{14}H_{10}O_2$	15.51	1.52
$C_{14}H_{11}NO$	15.89	1.38
$C_{14}H_{12}N_2$	16.26	1.24
$C_{14}H_{14}O_2$	16.40	1.66
$C_{14}H_{13}NO$	16.77	1.52
$C_{15}H_{11}N_3$	17.15	1.38
$C_{15}H_{22}O$	16.62	1.49
$C_{15}H_{21}N$	16.99	1.36
$C_{16}H_{11}O$	17.51	1.64
$C_{16}H_{13}N$	17.88	1.50
$C_{16}H_{27}$	17.72	1.48
$C_{17}HN$	18.77	1.66
$C_{17}H_{15}$	18.61	1.63
$C_{18}H_3$	19.50	1.80
220		
$C_9H_{56}N_2O_4$	10.97	1.35
$C_9H_{32}N_2O_5$	11.34	1.19
$C_9H_8N_4O_5$	11.71	1.03
$C_{10}H_8N_2O_4$	11.85	1.44
$C_{10}H_9N_3O_3$	12.23	1.29
$C_{10}H_{12}N_4O_2$	12.60	1.13
$C_{10}H_{22}NO_4$	11.70	1.43
$C_{10}H_{24}N_2O_3$	12.07	1.27
$C_{11}H_{20}NO_4$	12.58	1.53
$C_{11}H_{12}N_2O_3$	12.96	1.38
$C_{11}H_4N_5O_2$	13.33	1.22
$C_{11}H_6N_4O$	13.71	1.07
$C_{11}H_{24}O_4$	12.43	1.51
$C_{12}H_8N_2O_2$	14.22	1.34
$C_{12}H_4N_4O$	14.60	1.19
$C_{12}H_{12}O_4$	13.32	1.62
$C_{12}H_4NO_3$	13.69	1.47
$C_{12}H_6N_2O_2$	14.06	1.32
$C_{12}H_8N_2O$	14.44	1.17
$C_{12}H_8N_4$	14.81	1.02
$C_{13}H_2NO_3$	14.58	1.59
$C_{13}H_4N_2O_2$	14.95	1.44
$C_{13}H_6N_2O$	15.33	1.30
$C_{13}H_8N_4$	15.70	1.15
$C_{13}H_{16}O_3$	14.42	1.57
$C_{13}H_{18}NO_2$	14.80	1.42
$C_{13}H_{20}N_2O$	15.17	1.27
$C_{13}H_{22}N_2$	15.54	1.13
$C_{14}H_6O_3$	15.31	1.69
$C_{14}H_8NO_2$	15.68	1.55
$C_{14}H_8N_2O$	16.06	1.41
$C_{14}H_{10}N_2$	16.43	1.27
$C_{14}H_{26}O_2$	15.53	1.52
$C_{14}H_{22}NO$	15.90	1.38
$C_{14}H_{24}N_2$	16.28	1.24
$C_{15}H_8O_2$	16.42	1.66
$C_{15}H_{10}NO$	16.79	1.52
$C_{15}H_{12}N_2$	17.16	1.38
$C_{15}H_{24}O$	16.63	1.50
$C_{15}H_{26}N$	17.01	1.36
$C_{16}H_{12}O$	17.52	1.64
$C_{16}H_{14}N$	17.90	1.51
$C_{16}H_{28}$	17.74	1.48
$C_{17}H_2N$	18.78	1.66
$C_{17}H_{16}$	18.63	1.64
$C_{18}H_4$	19.52	1.80
221		
$C_9H_{21}N_2O_4$	10.98	1.35
$C_9H_{23}N_3O_3$	11.36	1.19
$C_{10}H_9N_2O_4$	11.87	1.45
$C_{10}H_{11}N_2O_3$	12.24	1.29
$C_{10}H_{13}N_4O_2$	12.62	1.14
$C_{10}H_{23}NO_4$	11.71	1.43
$C_{11}HN_4O_2$	13.51	1.25
$C_{11}H_{13}NO_4$	12.60	1.53
$C_{11}H_{15}N_2O_3$	12.98	1.38
$C_{11}H_{15}N_3O_2$	13.35	1.23
$C_{11}H_{17}N_4O$	13.72	1.08
$C_{12}HN_2O_3$	13.86	1.49
$C_{12}H_3N_3O_2$	14.24	1.34
$C_{12}H_5N_4O$	14.61	1.20
$C_{12}H_{13}O_4$	13.33	1.62
$C_{12}H_{15}NO_3$	13.71	1.47
$C_{12}H_{17}N_2O_2$	14.08	1.32
$C_{12}H_{19}N_3O$	14.46	1.17
$C_{12}H_{21}N_4$	14.83	1.03
$C_{13}HO_4$	14.22	1.74
$C_{13}H_3NO_3$	14.60	1.59
$C_{13}H_5N_2O_2$	14.97	1.44
$C_{13}H_7N_3O$	15.34	1.30
$C_{13}H_9N_4$	15.72	1.16
$C_{13}H_{17}O_3$	14.44	1.57
$C_{13}H_{19}NO_2$	14.81	1.42
$C_{13}H_{21}N_2O$	15.19	1.28
$C_{13}H_{23}N_3$	15.56	1.13
$C_{14}H_9O_3$	15.33	1.69
$C_{14}H_{11}NO_2$	15.70	1.55
$C_{14}H_{13}N_2O$	16.07	1.41
$C_{14}H_{15}N_3$	16.45	1.27
$C_{14}H_{21}O_2$	15.54	1.53
$C_{14}H_{23}NO$	15.92	1.38
$C_{14}H_{25}N_2$	16.29	1.24
$C_{15}H_9O_2$	16.43	1.66
$C_{15}H_{11}NO$	16.81	1.52
$C_{15}H_{13}N_2$	17.18	1.39
$C_{15}H_{23}O$	16.65	1.50
$C_{15}H_{21}N$	17.02	1.36
$C_{16}HN_2$	18.07	1.54
$C_{16}H_9O$	17.54	1.64
$C_{16}H_{15}N$	17.91	1.51
$C_{16}H_{29}$	17.75	1.48
$C_{17}HO$	18.43	1.80
$C_{17}H_5N$	18.80	1.67
$C_{17}H_{17}$	18.64	1.64
$C_{18}H_5$	19.53	1.80
222		
$C_8H_{22}N_2O_4$	11.00	1.35
$C_{16}H_{10}N_2O_4$	11.89	1.45
$C_{16}H_{12}N_2O_3$	12.26	1.29
$C_{16}H_{14}N_4O_2$	12.63	1.14
$C_{11}H_{24}N_4O_2$	13.52	1.25
$C_{11}H_{22}NO_4$	12.62	1.53
$C_{11}H_{14}N_2O_3$	12.99	1.38
$C_{11}H_{16}N_3O_2$	13.37	1.23
$C_{11}H_{18}N_4O$	13.74	1.08
$C_{12}H_2N_2O_3$	13.88	1.49
$C_{12}H_4N_3O_2$	14.25	1.34
$C_{12}H_6N_4O$	14.63	1.20
$C_{12}H_{14}O_4$	13.35	1.62
$C_{12}H_{16}NO_3$	13.72	1.47
$C_{12}H_{18}N_2O_2$	14.10	1.32
$C_{12}H_{20}N_3O$	14.47	1.18
$C_{12}H_{22}N_4$	14.85	1.03
$C_{13}H_4O_4$	14.24	1.74
$C_{13}H_6NO_3$	14.61	1.59
$C_{13}H_8N_2O_2$	14.99	1.45
$C_{13}H_{10}N_3O$	15.36	1.30
$C_{13}H_{12}N_4$	15.73	1.16
$C_{13}H_{20}O_3$	14.45	1.57
$C_{13}H_{22}NO_2$	14.83	1.42
$C_{13}H_{24}N_2O$	15.20	1.28
$C_{13}H_{26}N_3$	15.58	1.14
$C_{14}H_6O_3$	15.34	1.70
$C_{14}H_8NO_2$	15.72	1.55
$C_{14}H_{10}N_2O$	16.09	1.41
$C_{14}H_{12}N_3$	16.47	1.27
$C_{14}H_{24}O_2$	15.56	1.53
$C_{14}H_{26}NO$	15.93	1.39
$C_{14}H_{28}N_2$	16.31	1.25
$C_{15}H_{10}O_2$	16.45	1.67
$C_{15}H_{12}NO$	16.82	1.53
$C_{15}H_{14}N_2$	17.20	1.39
$C_{15}H_{26}O$	16.66	1.50
$C_{15}H_{28}N$	17.04	1.36
$C_{16}H_2N_2$	18.09	1.54
$C_{16}H_4O$	17.55	1.65
$C_{16}H_{16}N$	17.93	1.51
$C_{16}H_{30}$	17.77	1.49
$C_{17}H_2O$	18.44	1.80
$C_{17}H_4N$	18.82	1.67
$C_{17}H_{18}$	18.66	1.64
$C_{18}H_6$	19.55	1.81
223		
$C_{10}H_{11}N_2O_4$	11.90	1.45
$C_{10}H_{13}N_3O_3$	12.28	1.29
$C_{10}H_{15}N_4O_2$	12.65	1.14
$C_{11}HN_3O_3$	13.16	1.40
$C_{11}H_3N_4O_2$	13.54	1.25
$C_{11}H_{15}NO_4$	12.63	1.53
$C_{11}H_{15}N_2O_3$	13.01	1.38
$C_{11}H_{17}N_3O_2$	13.38	1.23
$C_{11}H_{19}N_4O$	13.76	1.08
$C_{12}HNO_4$	13.52	1.65
$C_{12}H_3N_2O_3$	13.90	1.50
$C_{12}H_5N_3O_2$	14.27	1.35
$C_{12}H_7N_4O$	14.64	1.20
$C_{12}H_{15}O_4$	13.36	1.62
$C_{12}H_{17}NO_3$	13.74	1.47
$C_{12}H_{19}N_2O_2$	14.11	1.33
$C_{12}H_{21}N_3O$	14.49	1.18
$C_{12}H_{23}N_4$	14.86	1.03
$C_{13}H_5O_4$	14.25	1.74
$C_{13}H_7NO_3$	14.63	1.59
$C_{13}H_9N_2O_2$	15.00	1.45
$C_{13}H_{11}N_3O$	15.38	1.30
$C_{13}H_{13}N_4$	15.75	1.16
$C_{13}H_{21}O_3$	14.47	1.57
$C_{13}H_{23}NO_2$	14.84	1.43
$C_{13}H_{25}N_2O$	15.22	1.28
$C_{13}H_{27}N_3$	15.59	1.14
$C_{14}H_7O_3$	15.36	1.70
$C_{14}H_9NO_2$	15.73	1.56
$C_{14}H_{11}N_2O$	16.11	1.41
$C_{14}H_{13}N_3$	16.48	1.27
$C_{14}H_{25}O_2$	15.58	1.53
$C_{14}H_{27}NO$	15.95	1.39
$C_{14}H_{29}N_2$	16.32	1.25
$C_{15}HN_3$	17.37	1.42
$C_{15}H_{13}O_2$	16.46	1.67
$C_{15}H_{15}NO$	16.84	1.53
$C_{15}H_{17}N_2$	17.21	1.39
$C_{15}H_{27}O$	16.68	1.50
$C_{15}H_{29}N$	17.06	1.37
$C_{16}HNO$	17.73	1.68
$C_{16}H_3N_2$	18.10	1.54
$C_{16}H_{17}O$	17.57	1.65
$C_{16}H_{17}N$	17.94	1.52
$C_{16}H_{31}$	17.79	1.49
$C_{17}H_3O$	18.46	1.80
$C_{17}H_5N$	18.83	1.67
$C_{17}H_{19}$	18.67	1.64
$C_{18}H_7$	19.56	1.81
224		
$C_{10}H_{12}N_2O_4$	11.92	1.45
$C_{10}H_{14}N_3O_3$	12.29	1.30
$C_{10}H_{16}N_4O_2$	12.67	1.14
$C_{11}H_2N_2O_3$	13.18	1.40
$C_{11}H_4N_3O_2$	13.56	1.25
$C_{11}H_{14}NO_4$	12.65	1.54
$C_{11}H_{16}N_2O_3$	13.02	1.38
$C_{11}H_{18}N_3O_2$	13.40	1.23
$C_{11}H_{20}N_4O$	13.77	1.08
$C_{12}H_2NO_4$	13.54	1.65
$C_{12}H_4N_2O_3$	13.91	1.50
$C_{12}H_6N_3O_2$	14.29	1.35
$C_{12}H_8N_4O$	14.66	1.20
$C_{12}H_{16}O_4$	13.38	1.63
$C_{12}H_{18}NO_3$	13.75	1.48
$C_{12}H_{20}N_2O_2$	14.13	1.33
$C_{12}H_{22}N_3O$	14.50	1.18
$C_{12}H_{24}N_4$	14.88	1.03
$C_{13}H_6O_4$	14.27	1.74
$C_{13}H_8NO_3$	14.64	1.60
$C_{13}H_8N_2O_2$	15.02	1.45
$C_{13}H_{10}N_3O$	15.39	1.31
$C_{13}H_{12}N_4$	15.77	1.16
$C_{13}H_{20}O_3$	14.49	1.57
$C_{13}H_{22}NO_2$	14.86	1.43
$C_{13}H_{24}N_2O$	15.23	1.28
$C_{13}H_{26}N_3$	15.61	1.14
$C_{14}H_8O_3$	15.37	1.70
$C_{14}H_{10}NO_2$	15.75	1.56
$C_{14}H_{12}N_2O$	16.12	1.42
$C_{14}H_{14}N_3$	16.50	1.28
$C_{14}H_{26}O_2$	15.59	1.53

	P + 1	P + 2
$C_{14}H_{26}NO$	15.97	1.39
$C_{14}H_{18}N_2$	16.34	1.25
$C_{15}H_{22}N_3$	17.39	1.42
$C_{11}H_{15}O_3$	16.48	1.67
$C_{15}H_{44}NO$	16.85	1.53
$C_{13}H_{16}N_2$	17.23	1.40
$C_{13}H_{20}O$	16.70	1.51
$C_{15}H_{30}N$	17.07	1.37
$C_{16}H_{2}NO$	17.74	1.68
$C_{16}H_{4}N_2$	18.12	1.55
$C_{16}H_{16}O$	17.59	1.65
$C_{16}H_{18}N$	17.96	1.52
$C_{16}H_{32}$	17.80	1.49
$C_{17}H_{4}O$	18.47	1.81
$C_{17}H_{6}N$	18.85	1.68
$C_{17}H_{20}$	18.69	1.65
$C_{18}H_{8}$	19.58	1.81
225		
$C_{16}H_{13}N_2O_4$	11.93	1.45
$C_{16}H_{15}N_3O_3$	12.31	1.30
$C_{16}H_{17}N_4O_2$	12.68	1.14
$C_{11}HN_2O_4$	12.82	1.56
$C_{11}H_{5}N_3O_3$	13.20	1.41
$C_{11}H_{7}N_4O_2$	13.57	1.25
$C_{11}H_{15}NO_4$	12.66	1.54
$C_{11}H_{17}N_2O_3$	13.04	1.39
$C_{11}H_{19}N_4O_2$	13.41	1.23
$C_{11}H_{21}N_4O$	13.79	1.08
$C_{12}H_{5}NO_4$	13.55	1.65
$C_{12}H_{7}N_2O_3$	13.93	1.50
$C_{12}H_{9}N_3O_2$	14.30	1.35
$C_{12}H_{9}N_4O$	14.68	1.20
$C_{12}H_{17}O_4$	13.40	1.63
$C_{12}H_{19}NO_3$	13.77	1.48
$C_{12}H_{21}N_2O_2$	14.14	1.33
$C_{12}H_{23}N_3O$	14.52	1.18
$C_{12}H_{25}N_4$	14.89	1.04
$C_{13}H_{5}O_4$	14.28	1.75
$C_{13}H_{7}NO_3$	14.66	1.60
$C_{13}H_{9}N_2O_2$	15.03	1.45
$C_{13}H_{11}N_3O$	15.41	1.31
$C_{13}H_{13}N_4$	15.78	1.17
$C_{13}H_{21}O_3$	14.50	1.58
$C_{13}H_{23}NO_2$	14.88	1.43
$C_{13}H_{25}N_2O$	15.25	1.29
$C_{13}H_{27}N_3$	15.62	1.14
$C_{14}HN_4$	16.67	1.30
$C_{14}H_{9}O_3$	15.39	1.70
$C_{14}H_{11}NO_2$	15.76	1.56
$C_{14}H_{13}N_2O$	16.14	1.42
$C_{14}H_{15}N_3$	16.51	1.28
$C_{14}H_{25}O_2$	15.61	1.54
$C_{14}H_{27}NO$	15.98	1.39
$C_{14}H_{28}N_2$	16.36	1.25
$C_{15}HN_2O$	17.03	1.56
$C_{15}H_{3}N_3$	17.40	1.42
$C_{15}H_{13}O_2$	16.50	1.67
$C_{15}H_{15}NO$	16.87	1.54
$C_{15}H_{17}N_2$	17.24	1.40
$C_{15}H_{29}O$	16.71	1.51
$C_{15}H_{31}N$	17.09	1.37
$C_{16}HO_2$	17.38	1.82
$C_{16}H_{3}NO$	17.76	1.68
$C_{16}H_{5}N_2$	18.13	1.55
$C_{16}H_{17}O$	17.60	1.66
$C_{16}H_{19}N$	17.98	1.52
$C_{16}H_{33}$	17.82	1.49
$C_{17}H_{5}O$	18.49	1.81
$C_{17}H_{7}N$	18.86	1.68
$C_{17}H_{21}$	18.71	1.65
$C_{18}H_{9}$	19.60	1.81
226		
$C_{10}H_{14}N_2O_4$	11.95	1.46
$C_{10}H_{16}N_3O_3$	12.32	1.30
$C_{10}H_{18}N_4O_2$	12.70	1.15
$C_{11}H_{2}N_2O_4$	12.84	1.56
$C_{11}H_{4}N_3O_3$	13.21	1.41
$C_{11}H_{6}N_4O_2$	13.59	1.26
$C_{11}H_{14}NO_4$	12.68	1.54
$C_{11}H_{16}N_2O_3$	13.06	1.39
$C_{11}H_{18}N_3O_2$	13.43	1.24
$C_{11}H_{20}N_4O$	13.80	1.09
$C_{12}H_{4}NO_4$	13.57	1.65
$C_{12}H_{6}N_2O_3$	13.94	1.50
$C_{12}H_{8}N_3O_2$	14.32	1.35
$C_{12}H_{10}N_4O$	14.69	1.21
$C_{12}H_{18}O_4$	13.41	1.63
$C_{12}H_{20}NO_3$	13.79	1.48
$C_{12}H_{22}N_2O_2$	14.16	1.33
$C_{12}H_{24}N_3O$	14.54	1.18
$C_{12}H_{26}N_4$	14.91	1.04
$C_{13}H_{6}O_4$	14.30	1.75
$C_{13}H_{8}NO_3$	14.68	1.60
$C_{13}H_{10}N_2O_2$	15.05	1.46
$C_{13}H_{12}N_3O$	15.42	1.31
$C_{13}H_{14}N_4$	15.80	1.17
$C_{13}H_{22}O_3$	14.52	1.58
$C_{13}H_{24}NO_2$	14.89	1.43
$C_{13}H_{26}N_2O$	15.27	1.29
$C_{13}H_{28}N_3$	15.64	1.15
$C_{14}H_{2}N_4$	16.69	1.31
$C_{14}H_{10}O_3$	15.41	1.71
$C_{14}H_{12}NO_2$	15.78	1.56
$C_{14}H_{14}N_2O$	16.15	1.42
$C_{14}H_{16}N_3$	16.53	1.28
$C_{14}H_{26}O_2$	15.62	1.54
$C_{14}H_{28}NO$	16.00	1.40
$C_{14}H_{30}N_2$	16.37	1.26
$C_{15}H_{2}N_2O$	17.04	1.56
$C_{15}H_{4}N_3$	17.42	1.43
$C_{15}H_{14}O_2$	16.51	1.68
$C_{15}H_{16}NO$	16.89	1.54
$C_{15}H_{18}N_2$	17.26	1.40
$C_{15}H_{30}O$	16.73	1.51
$C_{15}H_{32}N$	17.10	1.37
$C_{16}H_{32}O_2$	17.40	1.82
$C_{16}H_{4}NO$	17.77	1.69
$C_{16}H_{6}N_2$	18.15	1.55
$C_{16}H_{18}O$	17.62	1.66
$C_{16}H_{20}N$	17.99	1.52
$C_{16}H_{34}$	17.83	1.50
$C_{17}H_{6}O$	18.51	1.81
$C_{17}H_{8}N$	18.88	1.68
$C_{17}H_{22}$	18.72	1.65
$C_{18}H_{10}$	19.61	1.82
227		
$C_{10}H_{13}N_2O_4$	11.97	1.46
$C_{10}H_{15}N_3O_3$	12.34	1.30
$C_{10}H_{17}N_4O_2$	12.71	1.15
$C_{11}H_{3}N_2O_4$	12.85	1.56
$C_{11}H_{5}N_3O_3$	13.23	1.41
$C_{11}H_{7}N_4O_2$	13.60	1.26
$C_{11}H_{17}NO_4$	12.70	1.54
$C_{11}H_{19}N_2O_3$	13.07	1.39
$C_{11}H_{21}N_3O_2$	13.45	1.24
$C_{11}H_{23}N_4O$	13.82	1.09
$C_{12}H_{7}NO_4$	13.59	1.65
$C_{12}H_{9}N_2O_3$	13.96	1.50
$C_{12}H_{11}N_3O_2$	14.33	1.36
$C_{12}H_{13}N_4O$	14.71	1.21
$C_{12}H_{21}O_4$	13.43	1.63
$C_{12}H_{23}NO_3$	13.80	1.48
$C_{12}H_{25}N_2O_2$	14.18	1.33
$C_{12}H_{27}N_3O$	14.55	1.19
$C_{12}H_{29}N_4$	14.93	1.04
$C_{13}H_{9}O_4$	14.32	1.75
$C_{13}H_{11}NO_3$	14.69	1.60
$C_{13}H_{13}N_2O_2$	15.07	1.46
$C_{13}H_{15}N_3O$	15.44	1.31
$C_{13}H_{17}N_4$	15.81	1.17
$C_{13}H_{25}O_3$	14.53	1.58
$C_{13}H_{27}NO_2$	14.91	1.44
$C_{13}H_{29}N_2O$	15.28	1.29
$C_{13}H_{31}N_3$	15.66	1.15
$C_{14}HNO_4$	16.33	1.45
$C_{14}H_{3}N_2O$	16.70	1.31
$C_{14}H_{11}O_3$	15.42	1.71
$C_{14}H_{13}NO_2$	15.80	1.57
$C_{14}H_{15}N_2O$	16.17	1.42
$C_{14}H_{17}N_3$	16.55	1.28
$C_{14}H_{27}O_2$	15.64	1.54
$C_{14}H_{29}NO$	16.01	1.40
$C_{14}H_{31}N_2$	16.39	1.26
$C_{15}HNO_2$	16.69	1.70
$C_{15}H_{3}N_2O$	17.06	1.57
$C_{15}H_{5}N_3$	17.43	1.43
$C_{15}H_{15}O_2$	16.53	1.68
$C_{15}H_{17}NO$	16.90	1.54
$C_{15}H_{19}N_2$	17.28	1.40
$C_{15}H_{31}O$	16.74	1.51
$C_{15}H_{33}N$	17.12	1.38
$C_{16}H_{3}O_2$	17.42	1.82
$C_{16}H_{5}NO$	17.79	1.69
$C_{16}H_{7}N_2$	18.17	1.55
$C_{16}H_{19}O$	17.63	1.66
$C_{16}H_{21}N$	18.01	1.53
$C_{17}H_{5}O$	18.52	1.82
$C_{17}H_{9}N$	18.90	1.69
$C_{17}H_{23}$	18.74	1.66
$C_{18}H_{11}$	19.63	1.82
228		
$C_{10}H_{16}N_2O_4$	11.98	1.46
$C_{10}H_{18}N_3O_3$	12.36	1.30
$C_{10}H_{20}N_4O_2$	12.73	1.15
$C_{11}H_{4}N_2O_4$	12.87	1.56
$C_{11}H_{6}N_3O_3$	13.24	1.41
$C_{11}H_{8}N_4O_2$	13.62	1.26
$C_{11}H_{18}NO_4$	12.71	1.55
$C_{11}H_{20}N_2O_3$	13.09	1.39
$C_{11}H_{22}N_3O_2$	13.46	1.24
$C_{11}H_{24}N_4O$	13.84	1.09
$C_{12}H_{8}NO_4$	13.60	1.66
$C_{12}H_{10}N_2O_3$	13.98	1.51
$C_{12}H_{12}N_3O_2$	14.35	1.36
$C_{12}H_{14}N_4O$	14.72	1.21
$C_{12}H_{22}O_4$	13.44	1.64
$C_{12}H_{24}NO_3$	13.82	1.49
$C_{12}H_{26}N_2O_2$	14.19	1.34
$C_{12}H_{28}N_3O$	14.57	1.19
$C_{12}H_{30}N_4$	14.94	1.04
$C_{13}H_{10}O_4$	14.33	1.75
$C_{13}H_{12}NO_3$	14.71	1.61
$C_{13}H_{14}N_2O_2$	15.08	1.46
$C_{13}H_{16}N_3O$	15.46	1.32
$C_{13}H_{18}N_4$	15.83	1.17
$C_{13}H_{26}O_3$	14.55	1.58
$C_{13}H_{28}NO_2$	14.92	1.44
$C_{13}H_{30}N_2O$	15.30	1.29
$C_{13}H_{32}N_3$	15.67	1.15
$C_{14}H_{2}N_2O$	16.34	1.45
$C_{14}H_{4}N_4$	16.72	1.31
$C_{14}H_{12}O_3$	15.44	1.71
$C_{14}H_{14}NO_2$	15.81	1.57
$C_{14}H_{16}N_2O$	16.19	1.43
$C_{14}H_{18}N_3$	16.56	1.29
$C_{14}H_{28}O_2$	15.66	1.54
$C_{14}H_{30}NO$	16.03	1.40
$C_{14}H_{32}N_2$	16.40	1.26
$C_{15}H_{2}NO_2$	16.70	1.71
$C_{15}H_{4}N_2O$	17.08	1.57
$C_{15}H_{6}N_3$	17.45	1.43
$C_{15}H_{16}O_2$	16.54	1.68
$C_{15}H_{18}NO$	16.92	1.54
$C_{15}H_{20}N_2$	17.29	1.41
$C_{15}H_{32}O$	16.76	1.52
$C_{16}H_{4}O_2$	17.43	1.83
$C_{16}H_{6}NO$	17.81	1.69
$C_{16}H_{8}N_2$	18.18	1.56
$C_{16}H_{20}O$	17.65	1.66
$C_{16}H_{22}N$	18.02	1.53
$C_{17}H_{6}O$	18.54	1.82
$C_{17}H_{10}N$	18.91	1.69
$C_{17}H_{24}$	18.75	1.66
$C_{18}H_{12}$	19.64	1.82
229		
$C_{10}H_{17}N_2O_4$	12.00	1.46
$C_{10}H_{19}N_3O_3$	12.37	1.31
$C_{10}H_{21}N_4O_2$	12.75	1.15
$C_{11}H_{5}N_2O_4$	12.89	1.57
$C_{11}H_{7}N_3O_3$	13.26	1.41
$C_{11}H_{9}N_4O_2$	13.64	1.26
$C_{11}H_{19}NO_4$	12.73	1.55
$C_{11}H_{21}N_2O_3$	13.10	1.39
$C_{11}H_{23}N_3O_2$	13.48	1.24
$C_{11}H_{25}N_4O$	13.85	1.09
$C_{12}H_{9}NO_4$	13.62	1.66
$C_{12}H_{11}N_2O_3$	13.99	1.51

	P + 1	P + 2
$C_{12}H_{11}N_3O_2$	14.37	1.36
$C_{13}H_{18}N_4O$	14.74	1.21
$C_{12}H_{21}O_4$	13.46	1.64
$C_{12}H_{23}NO_3$	13.83	1.49
$C_{12}H_{25}N_2O_2$	14.21	1.34
$C_{12}H_{27}N_3O$	14.58	1.19
$C_{12}H_{29}N_4$	14.96	1.05
$C_{13}HN_4O$	15.63	1.34
$C_{13}H_8O_4$	14.35	1.76
$C_{13}H_{17}NO_3$	14.72	1.61
$C_{13}H_{19}N_2O_2$	15.10	1.46
$C_{13}H_{21}N_3O$	15.47	1.32
$C_{13}H_{17}N_4$	15.85	1.18
$C_{13}H_{29}O_3$	14.57	1.59
$C_{13}H_{27}NO_2$	14.94	1.44
$C_{13}H_{29}N_2O$	15.31	1.30
$C_{13}H_{31}N_3$	15.69	1.15
$C_{14}HN_2O_2$	15.99	1.60
$C_{14}H_5N_3O$	16.36	1.45
$C_{14}H_5N_4$	16.73	1.32
$C_{14}H_9O_3$	15.45	1.71
$C_{14}H_{11}NO_2$	15.83	1.57
$C_{14}H_{13}N_2O$	16.20	1.43
$C_{14}H_{15}N_3$	16.58	1.29
$C_{14}H_{25}O_3$	15.67	1.55
$C_{14}H_{31}NO$	16.05	1.41
$C_{15}H_{10}S$	16.34	1.85
$C_{15}H_{20}NO_2$	16.72	1.71
$C_{15}H_{12}N_2O$	17.09	1.57
$C_{15}H_{14}N_3$	17.47	1.44
$C_{15}H_{17}O_2$	16.56	1.68
$C_{15}H_{19}NO$	16.93	1.55
$C_{15}H_{21}N_2$	17.31	1.41
$C_{16}H_{24}O_2$	17.45	1.83
$C_{16}H_{19}NO$	17.82	1.69
$C_{16}H_{23}N_2$	18.20	1.56
$C_{16}H_{21}O$	17.67	1.67
$C_{16}H_{23}N$	18.04	1.53
$C_{17}H_9O$	18.55	1.82
$C_{17}H_{11}N$	18.93	1.69
$C_{17}H_{25}$	18.77	1.66
$C_{18}H_{13}$	19.66	1.83
$C_{19}H$	20.55	2.00

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$C_{10}H_{18}N_2O_4$	12.01	1.46
$C_{12}H_{26}N_2O_3$	12.39	1.31
$C_{12}H_{22}N_4O_2$	12.76	1.15
$C_{11}H_{22}N_2O_4$	12.90	1.57
$C_{11}H_{18}N_3O_3$	13.28	1.42
$C_{11}H_{20}N_4O_2$	13.65	1.27
$C_{11}H_{28}NO_4$	12.74	1.55
$C_{11}H_{22}N_2O_3$	13.12	1.40
$C_{11}H_{24}N_3O_2$	13.49	1.24
$C_{11}H_{26}N_4O$	13.87	1.09
$C_{12}H_{20}NO_4$	13.63	1.66
$C_{12}H_{18}N_2O_3$	14.01	1.51
$C_{12}H_{22}N_3O_2$	14.38	1.36
$C_{12}H_{24}N_4O$	14.76	1.22
$C_{12}H_{22}O_4$	13.48	1.64
$C_{12}H_{24}NO_3$	13.85	1.49
$C_{12}H_{26}N_2O_2$	14.22	1.34
$C_{12}H_{28}N_3O$	14.60	1.19
$C_{12}H_{30}N_4$	14.97	1.05
$C_{13}H_2N_4O$	15.65	1.35
$C_{13}H_{10}O_4$	14.36	1.76
$C_{13}H_{19}NO_3$	14.74	1.61
$C_{13}H_{21}N_2O_2$	15.11	1.47
$C_{13}H_{23}N_3O$	15.49	1.32
$C_{13}H_{25}N_4$	15.86	1.18
$C_{13}H_{26}O_3$	14.58	1.59
$C_{13}H_{28}NO_2$	14.96	1.44
$C_{13}H_{30}N_2O$	15.33	1.30
$C_{14}H_2N_2O_2$	16.00	1.60
$C_{14}H_4N_3O$	16.38	1.46
$C_{14}H_6N_4$	16.75	1.32
$C_{14}H_{14}O_3$	15.47	1.72
$C_{14}H_{16}NO_2$	15.84	1.57
$C_{14}H_{18}N_2O$	16.22	1.43
$C_{14}H_{20}N_3$	16.59	1.29
$C_{14}H_{30}O_2$	15.69	1.55
$C_{15}H_3O_3$	16.36	1.85
$C_{15}H_5NO_2$	16.73	1.71
$C_{15}H_7N_2O$	17.11	1.57
$C_{15}H_9N_3$	17.48	1.44
$C_{15}H_{17}O_2$	16.58	1.69
$C_{15}H_{19}NO$	16.95	1.55
$C_{15}H_{21}N_2$	17.32	1.41
$C_{16}H_8O_2$	17.46	1.83
$C_{16}H_{10}NO$	17.84	1.70
$C_{16}H_{12}N_2$	18.21	1.56
$C_{16}H_{23}O$	17.68	1.67
$C_{16}H_{24}N$	18.06	1.54
$C_{17}H_{20}O$	18.57	1.83
$C_{17}H_{22}N$	18.94	1.69
$C_{17}H_{26}$	18.79	1.67
$C_{18}H_{14}$	19.68	1.83
$C_{19}H_2$	20.56	2.00

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$C_{10}H_{17}N_3O_4$	12.03	1.47
$C_{12}H_{17}N_3O_3$	12.40	1.31
$C_{12}H_{19}N_4O_2$	12.78	1.16
$C_{11}H_{17}N_2O_4$	12.92	1.57
$C_{11}H_{19}N_3O_3$	13.29	1.42
$C_{11}H_{11}N_4O_2$	13.67	1.27
$C_{11}H_{21}NO_4$	12.76	1.55
$C_{11}H_{23}N_2O_3$	13.14	1.40
$C_{11}H_{25}N_3O_2$	13.51	1.25
$C_{11}H_{27}N_4O$	13.88	1.10
$C_{12}H_9NO_4$	13.65	1.66
$C_{12}H_{11}N_2O_3$	14.02	1.51
$C_{12}H_{13}N_3O_2$	14.40	1.37
$C_{12}H_{15}N_4O$	14.77	1.22
$C_{12}H_{23}O_4$	13.49	1.64
$C_{12}H_{25}NO_3$	13.87	1.49
$C_{12}H_{27}N_2O_2$	14.24	1.34
$C_{12}H_{29}N_3O$	14.62	1.20
$C_{13}HN_3O_2$	15.29	1.49
$C_{13}H_5N_4O$	15.66	1.35
$C_{13}H_{13}O_4$	14.38	1.76
$C_{13}H_{15}NO_3$	14.76	1.61
$C_{13}H_{17}N_2O_2$	15.13	1.47
$C_{13}H_{19}N_3O$	15.50	1.32
$C_{13}H_{21}N_4$	15.88	1.18
$C_{13}H_{25}O_3$	14.60	1.59
$C_{13}H_{23}NO_2$	14.97	1.45
$C_{14}HNO_3$	15.64	1.74
$C_{14}H_3N_2O_2$	16.02	1.60
$C_{14}H_5N_3O$	16.39	1.46
$C_{14}H_7N_4$	16.77	1.32
$C_{14}H_{15}O_3$	15.49	1.72
$C_{14}H_{17}NO_2$	15.86	1.58
$C_{14}H_{19}N_2O$	16.23	1.44
$C_{14}H_{21}N_3$	16.61	1.30
$C_{15}H_5O_3$	16.37	1.85
$C_{15}H_7NO_2$	16.75	1.72
$C_{15}H_9N_2O$	17.12	1.58
$C_{15}H_{11}N_3$	17.50	1.44
$C_{15}H_{19}O_2$	16.59	1.69
$C_{15}H_{21}NO$	16.97	1.55
$C_{15}H_{23}N_2$	17.34	1.41
$C_{16}H_7O_2$	17.48	1.84
$C_{16}H_9NO$	17.85	1.70
$C_{16}H_{11}N_2$	18.23	1.57
$C_{16}H_{23}O$	17.70	1.67
$C_{16}H_{25}N$	18.07	1.54
$C_{17}H_{11}O$	18.59	1.83
$C_{17}H_{13}N$	18.96	1.70
$C_{17}H_{27}$	18.80	1.67
$C_{18}HN$	19.85	1.86
$C_{18}H_{15}$	19.69	1.83
$C_{19}H_3$	20.58	2.01

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$C_{10}H_{20}N_2O_4$	12.05	1.47
$C_{10}H_{22}N_3O_3$	12.42	1.31
$C_{10}H_{24}N_4O_2$	12.79	1.16
$C_{11}H_{26}N_2O_4$	12.93	1.57
$C_{11}H_{18}N_3O_3$	13.31	1.42
$C_{11}H_{20}N_4O_2$	13.68	1.27
$C_{11}H_{28}NO_4$	12.78	1.55
$C_{11}H_{24}N_2O_3$	13.15	1.40
$C_{11}H_{26}N_3O_2$	13.53	1.25
$C_{11}H_{28}N_4O$	13.90	1.10
$C_{12}H_{10}NO_4$	13.67	1.66
$C_{12}H_{12}N_2O$	14.04	1.52
$C_{12}H_{14}N_3O_2$	14.41	1.37
$C_{12}H_{16}N_4O$	14.79	1.22
$C_{12}H_{24}O_4$	13.51	1.64
$C_{12}H_{26}NO_3$	13.88	1.49
$C_{12}H_{28}N_2O_2$	14.26	1.35
$C_{12}H_{30}N_3O$	15.30	1.49
$C_{13}H_4N_4O$	15.68	1.35
$C_{13}H_{12}O_4$	14.40	1.76
$C_{13}H_{14}NO_3$	14.77	1.62
$C_{13}H_{16}N_2O_2$	15.15	1.47
$C_{13}H_{18}N_3O$	15.52	1.33
$C_{13}H_{20}N_4$	15.89	1.18
$C_{13}H_{28}O_3$	14.61	1.59
$C_{14}H_2NO_3$	15.66	1.75
$C_{14}H_4N_2O_2$	16.03	1.60
$C_{14}H_6N_3O$	16.41	1.46
$C_{14}H_8N_4$	16.78	1.32
$C_{14}H_{16}O_3$	15.50	1.72
$C_{14}H_{18}NO_2$	15.88	1.58
$C_{14}H_{20}N_2O$	16.25	1.44
$C_{14}H_{22}N_3$	16.63	1.30
$C_{15}H_6O_3$	16.39	1.86
$C_{15}H_8NO_2$	16.77	1.72
$C_{15}H_8N_2O$	17.14	1.58
$C_{15}H_{10}N_3$	17.51	1.44
$C_{15}H_{26}O_2$	16.61	1.69
$C_{15}H_{28}NO$	16.98	1.55
$C_{15}H_{30}N_2$	17.36	1.42
$C_{16}H_{18}O_2$	17.50	1.84
$C_{16}H_{20}NO$	17.87	1.70
$C_{16}H_{22}N_2$	18.25	1.57
$C_{16}H_{24}O$	17.71	1.68
$C_{16}H_{26}N$	18.09	1.54
$C_{17}H_{25}O$	18.60	1.83
$C_{17}H_{27}N$	18.98	1.70
$C_{17}H_{29}$	18.82	1.67
$C_{18}H_{27}N$	19.86	1.87
$C_{18}H_{25}$	19.71	1.84
$C_{19}H_4$	20.60	2.01

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$C_{10}H_{21}N_2O_4$	12.06	1.47
$C_{10}H_{23}N_3O_3$	12.44	1.31
$C_{10}H_{25}N_4O_2$	12.81	1.16
$C_{11}H_{25}N_2O_4$	12.95	1.57
$C_{11}H_{17}N_3O_3$	13.32	1.42
$C_{11}H_{19}N_4O_2$	13.70	1.27
$C_{11}H_{27}NO_4$	12.79	1.56
$C_{11}H_{25}N_2O_3$	13.17	1.40
$C_{11}H_{27}N_3O_2$	13.54	1.25
$C_{12}HN_4O_2$	14.59	1.39
$C_{12}H_{11}NO_4$	13.68	1.67
$C_{12}H_{13}N_2O_3$	14.06	1.52
$C_{12}H_{15}N_3O_2$	14.43	1.37
$C_{12}H_{17}N_4O$	14.80	1.22
$C_{12}H_{25}O_4$	13.52	1.65
$C_{12}H_{27}NO_3$	13.90	1.50
$C_{12}H_{29}N_2O_2$	14.94	1.64
$C_{12}H_{31}N_3O$	15.32	1.50
$C_{13}H_3N_4O$	15.69	1.35
$C_{13}H_{13}O_4$	14.41	1.76
$C_{13}H_{15}NO_3$	14.79	1.62
$C_{13}H_{17}N_2O_2$	15.16	1.47
$C_{13}H_{19}N_3O$	15.54	1.33
$C_{13}H_{21}N_4$	15.91	1.19
$C_{14}HO_4$	15.30	1.89
$C_{14}H_3NO_3$	15.68	1.75
$C_{14}H_5N_2O_2$	16.05	1.61
$C_{14}H_7N_3O$	16.42	1.47
$C_{14}H_9N_4$	16.80	1.33
$C_{14}H_{17}O_3$	15.52	1.72
$C_{14}H_{19}NO_2$	15.89	1.58
$C_{14}H_{21}N_2O$	16.27	1.44
$C_{14}H_{23}N_3$	16.64	1.30
$C_{15}H_7O_3$	16.41	1.86
$C_{15}H_9NO_2$	16.78	1.72
$C_{15}H_9N_2O$	17.16	1.58
$C_{15}H_{11}N_3$	17.53	1.45
$C_{15}H_{21}O_2$	16.62	1.70
$C_{15}H_{23}NO$	17.00	1.56
$C_{15}H_{25}N_2$	17.37	1.42
$C_{16}H_9O_2$	17.51	1.84
$C_{16}H_{11}NO$	17.89	1.71
$C_{16}H_{13}N_2$	18.26	1.57
$C_{16}H_{25}O$	17.73	1.68
$C_{16}H_{27}N$	18.10	1.54

	P + 1	P + 2
$C_{17}HN_5$	19.15	1.73
$C_{17}H_{13}O$	18.62	1.83
$C_{17}H_{15}N$	18.99	1.70
$C_{17}H_{23}$	18.83	1.67
$C_{18}HO$	19.51	2.00
$C_{18}H_3N$	19.88	1.87
$C_{18}H_{17}$	19.72	1.84
$C_{19}H_5$	20.61	2.01
234		
$C_{10}H_{22}N_2O_4$	12.08	1.47
$C_{10}H_{24}N_2O_3$	12.45	1.32
$C_{10}H_{26}N_4O_2$	12.83	1.16
$C_{11}H_{10}N_2O_4$	12.97	1.58
$C_{11}H_{12}N_3O_3$	13.34	1.42
$C_{11}H_{14}N_4O_2$	13.72	1.27
$C_{11}H_{24}NO_4$	12.81	1.56
$C_{11}H_{26}N_2O_3$	13.18	1.40
$C_{12}H_2N_4O_2$	14.60	1.39
$C_{12}H_{12}NO_4$	13.70	1.67
$C_{12}H_{14}N_3O_3$	14.07	1.52
$C_{12}H_{16}N_5O_2$	14.45	1.37
$C_{12}H_{18}N_4O$	14.82	1.23
$C_{12}H_{26}O_4$	13.54	1.65
$C_{13}H_2N_2O_3$	14.96	1.64
$C_{13}H_4N_3O_2$	15.33	1.50
$C_{13}H_6N_4O$	15.71	1.36
$C_{13}H_{14}O_4$	14.43	1.77
$C_{13}H_{16}NO_3$	14.80	1.62
$C_{13}H_{18}N_2O_2$	15.18	1.48
$C_{13}H_{20}N_3O$	15.55	1.33
$C_{13}H_{22}N_4$	15.93	1.19
$C_{14}H_5O_4$	15.32	1.89
$C_{14}H_4NO_3$	15.69	1.75
$C_{14}H_6N_2O_2$	16.07	1.61
$C_{14}H_8N_3O$	16.44	1.47
$C_{14}H_{10}N_4$	16.81	1.33
$C_{14}H_{18}O_3$	15.53	1.73
$C_{14}H_{20}NO_2$	15.91	1.58
$C_{14}H_{22}N_2O$	16.28	1.44
$C_{14}H_{24}N_3$	16.66	1.30
$C_{15}H_6O_3$	16.42	1.86
$C_{15}H_8NO_2$	16.80	1.72
$C_{15}H_{10}N_2O$	17.17	1.59
$C_{15}H_{12}N_3$	17.55	1.45
$C_{15}H_{22}O_2$	16.64	1.70
$C_{15}H_{24}NO$	17.01	1.56
$C_{15}H_{26}N_2$	17.39	1.42
$C_{16}H_{10}O_2$	17.53	1.84
$C_{16}H_{12}NO$	17.90	1.71
$C_{16}H_{14}N_2$	18.28	1.58
$C_{16}H_{26}O$	17.75	1.68
$C_{16}H_{28}N$	18.12	1.55
$C_{17}H_2N_2$	19.17	1.74
$C_{17}H_{14}O$	18.63	1.86
$C_{17}H_{16}N$	19.01	1.71
$C_{17}H_{30}$	18.85	1.68
$C_{18}H_2O$	19.52	2.00
$C_{18}H_4N$	19.90	1.87
$C_{18}H_{18}$	19.74	1.84
$C_{19}H_6$	20.63	2.02
235		
$C_{10}H_{23}N_2O_4$	12.09	1.47
$C_{10}H_{25}N_3O_3$	12.47	1.32
$C_{11}H_{11}N_2O_4$	12.98	1.58
$C_{11}H_{13}N_3O_3$	13.36	1.43
$C_{11}H_{15}N_4O_2$	13.73	1.28
$C_{11}H_{25}NO_4$	12.82	1.56
$C_{12}HN_2O_3$	14.25	1.54
$C_{12}H_3N_3O_2$	14.62	1.40
$C_{12}H_{13}NO_4$	13.71	1.67
$C_{12}H_{15}N_2O_3$	14.09	1.52
$C_{12}H_{17}N_3O_2$	14.46	1.37
$C_{12}H_{19}N_4O$	14.84	1.23
$C_{12}HNO_4$	14.60	1.79
$C_{13}H_9N_2O_3$	14.98	1.65
$C_{13}H_5N_3O_2$	15.35	1.50
$C_{13}H_7N_4O$	15.73	1.36
$C_{13}H_{15}O_4$	14.44	1.77
$C_{13}H_{17}NO_3$	14.82	1.62
$C_{13}H_{19}N_2O_2$	15.19	1.48
$C_{13}H_{21}N_3O$	15.57	1.33
$C_{13}H_{23}N_4$	15.94	1.19
$C_{14}H_9O_4$	15.33	1.90
$C_{14}H_8NO_3$	15.71	1.75
$C_{14}H_{10}N_2O_2$	16.08	1.61
$C_{14}H_{12}N_3O$	16.46	1.47
$C_{14}H_{14}N_4$	16.83	1.33
$C_{14}H_{19}O_3$	15.55	1.73
$C_{14}H_{21}NO_2$	15.92	1.59
$C_{14}H_{23}N_2O$	16.30	1.45
$C_{14}H_{25}N_3$	16.67	1.31
$C_{15}H_7O_3$	16.44	1.86
$C_{15}H_9NO_2$	16.81	1.73
$C_{15}H_{11}N_2O$	17.19	1.59
$C_{15}H_{13}N_3$	17.56	1.44
$C_{15}H_{23}O_2$	16.66	1.70
$C_{15}H_{25}NO$	17.03	1.56
$C_{15}H_{27}N_2$	17.40	1.43
$C_{16}HN_3$	18.45	1.61
$C_{16}H_{11}O_2$	17.54	1.85
$C_{16}H_{13}NO$	17.92	1.71
$C_{16}H_{15}N_2$	18.29	1.58
$C_{16}H_{27}O$	17.76	1.68
$C_{16}H_{29}N$	18.14	1.55
$C_{17}HNO$	18.81	1.87
$C_{17}H_3N_2$	19.18	1.74
$C_{17}H_{15}O$	18.65	1.84
$C_{17}H_{17}N$	19.02	1.71
$C_{17}H_{31}$	18.87	1.68
$C_{18}H_3O$	19.54	2.00
$C_{18}H_5N$	19.91	1.88
$C_{18}H_{19}$	19.76	1.85
$C_{19}H_7$	20.64	2.02
236		
$C_9H_{24}N_2O_4$	12.11	1.48
$C_{11}H_{12}N_2O_4$	13.00	1.58
$C_{11}H_{14}N_3O_3$	13.37	1.43
$C_{11}H_{16}N_4O_2$	13.75	1.28
$C_{12}H_4N_3O_3$	14.26	1.55
$C_{12}H_6N_4O_2$	14.64	1.40
$C_{12}H_{14}NO_4$	13.73	1.67
$C_{12}H_{16}N_2O_3$	14.10	1.52
$C_{12}H_{18}N_3O_2$	14.48	1.38
$C_{12}H_{20}N_4O$	14.85	1.23
$C_{13}H_8NO_4$	14.62	1.79
$C_{13}H_4N_2O_3$	14.99	1.65
$C_{13}H_6N_3O_2$	15.37	1.50
$C_{13}H_8N_4O$	15.74	1.36
$C_{13}H_{16}O_4$	14.46	1.77
$C_{13}H_{18}NO_3$	14.84	1.63
$C_{13}H_{20}N_2O_2$	15.21	1.48
$C_{13}H_{22}N_3O$	15.58	1.34
$C_{13}H_{24}N_4$	15.96	1.19
$C_{14}H_8O_4$	15.35	1.90
$C_{14}H_7NO_3$	15.72	1.76
$C_{14}H_9N_2O_2$	16.10	1.61
$C_{14}H_{11}N_3O$	16.47	1.47
$C_{14}H_{13}N_4$	16.85	1.33
$C_{14}H_{20}O_3$	15.57	1.73
$C_{14}H_{22}NO_2$	15.94	1.59
$C_{14}H_{24}N_2O$	16.31	1.45
$C_{14}H_{26}N_3$	16.69	1.31
$C_{15}H_8O_3$	16.45	1.87
$C_{15}H_{10}NO_2$	16.83	1.73
$C_{15}H_{12}N_2O$	17.20	1.59
$C_{15}H_{14}N_3$	17.58	1.46
$C_{15}H_{24}O_2$	16.67	1.70
$C_{15}H_{26}NO$	17.05	1.56
$C_{15}H_{28}N_2$	17.42	1.43
$C_{16}H_2N_3$	18.47	1.61
$C_{16}H_{12}O_2$	17.56	1.85
$C_{16}H_{14}NO$	17.93	1.71
$C_{16}H_{16}N_2$	18.31	1.58
$C_{16}H_{28}O$	17.78	1.69
$C_{16}H_{30}N$	18.15	1.55
$C_{17}H_2NO$	18.82	1.87
$C_{17}H_4N_2$	19.20	1.74
$C_{17}H_{16}O$	18.67	1.84
$C_{17}H_{18}N$	19.04	1.71
$C_{17}H_{32}$	18.88	1.68
$C_{18}H_4O$	19.55	2.01
$C_{18}H_6N$	19.93	1.88
$C_{18}H_{20}$	19.77	1.85
$C_{19}H_8$	20.66	2.02
237		
$C_{11}H_3N_2O_4$	13.01	1.58
$C_{11}H_5N_3O_3$	13.39	1.43
$C_{11}H_7N_4O_2$	13.76	1.28
$C_{12}N_2O_4$	13.90	1.70
$C_{12}H_3N_2O_3$	19.28	1.55
$C_{12}H_5N_3O_2$	14.65	1.40
$C_{12}H_{15}NO_4$	13.75	1.68
$C_{12}H_{17}N_2O_3$	14.12	1.53
$C_{12}H_{19}N_3O_2$	14.49	1.38
$C_{12}H_{21}N_4O$	14.87	1.23
$C_{13}H_5NO_4$	14.63	1.80
$C_{13}H_7N_2O_3$	15.01	1.65
$C_{13}H_9N_3O_2$	15.38	1.51
$C_{13}H_{11}N_4O$	15.76	1.36
$C_{13}H_{17}O_4$	14.48	1.77
$C_{13}H_{19}NO_3$	14.85	1.63
$C_{13}H_{21}N_2O_2$	15.23	1.48
$C_{13}H_{23}N_3O$	15.60	1.34
$C_{13}H_{25}N_4$	15.97	1.20
$C_{14}H_9O_4$	15.37	1.90
$C_{14}H_7NO_3$	15.74	1.76
$C_{14}H_9N_2O_2$	16.11	1.62
$C_{14}H_{11}N_3O$	16.49	1.48
$C_{14}H_{13}N_4$	16.86	1.34
$C_{14}H_{21}O_3$	15.58	1.73
$C_{14}H_{23}NO_2$	15.96	1.59
$C_{14}H_{25}N_2O$	16.33	1.45
$C_{14}H_{27}N_3$	16.71	1.31
$C_{15}HN_4$	17.75	1.49
$C_{15}H_9O_3$	16.47	1.87
$C_{15}H_{11}NO_2$	16.85	1.73
$C_{15}H_{13}N_2O$	17.22	1.59
$C_{15}H_{15}N_3$	17.59	1.46
$C_{15}H_{25}O_2$	16.69	1.71
$C_{15}H_{27}NO$	17.06	1.57
$C_{15}H_{29}N_2$	17.44	1.43
$C_{16}HN_2O$	18.11	1.75
$C_{16}H_3N_3$	18.48	1.61
$C_{16}H_{13}O_2$	17.58	1.85
$C_{16}H_{15}NO$	17.95	1.72
$C_{16}H_{17}N_2$	18.33	1.58
$C_{16}H_{29}O$	17.79	1.69
$C_{16}H_{31}N$	18.17	1.56
$C_{17}HO_3$	18.46	2.01
$C_{17}H_3NO$	18.84	1.88
$C_{17}H_5N_2$	19.21	1.75
$C_{17}H_{17}O$	18.68	1.85
$C_{17}H_{19}N$	19.06	1.72
$C_{17}H_{33}$	18.90	1.69
$C_{18}H_5O$	19.57	2.01
$C_{18}H_7N$	19.94	1.88
$C_{18}H_{21}$	19.79	1.85
$C_{19}H_9$	20.68	2.03
238		
$C_{11}H_4N_2O_4$	13.03	1.59
$C_{11}H_6N_3O_3$	13.40	1.43
$C_{11}H_8N_4O_2$	13.78	1.28
$C_{12}H_2N_2O_4$	13.92	1.70
$C_{12}H_4N_3O_3$	14.29	1.55
$C_{12}H_6N_4O_2$	14.67	1.40
$C_{12}H_{16}NO_4$	13.76	1.68
$C_{12}H_{18}N_2O_3$	14.14	1.53
$C_{12}H_{20}N_3O_2$	14.51	1.38
$C_{12}H_{22}N_4O$	14.88	1.24
$C_{13}H_6NO_4$	14.65	1.80
$C_{13}H_8N_2O_3$	15.02	1.65
$C_{13}H_{10}N_3O_2$	15.40	1.51
$C_{13}H_{12}N_4O$	15.77	1.37
$C_{13}H_{18}O_4$	14.49	1.78
$C_{13}H_{20}NO_3$	14.87	1.63
$C_{13}H_{22}N_2O_2$	15.24	1.49
$C_{13}H_{24}N_3O$	15.62	1.34
$C_{13}H_{26}N_4$	15.99	1.20
$C_{14}H_{10}O_4$	15.38	1.90
$C_{14}H_9NO_3$	15.76	1.76
$C_{14}H_{11}N_2O_2$	16.13	1.62
$C_{14}H_{13}N_3O$	16.50	1.48
$C_{14}H_{15}N_4$	16.88	1.34
$C_{14}H_{22}O_3$	15.60	1.74
$C_{14}H_{24}NO_2$	15.97	1.59
$C_{14}H_{26}N_2O$	16.35	1.45
$C_{14}H_{28}N_3$	16.72	1.31
$C_{15}H_2N_4$	17.77	1.49
$C_{15}H_{10}O_3$	16.49	1.87
$C_{15}H_{12}NO_2$	16.87	1.73
$C_{15}H_{14}N_2O$	17.24	1.59
$C_{15}H_{16}N_3$	17.62	1.46
$C_{15}H_{26}O_2$	16.71	1.71
$C_{15}H_{28}NO$	17.08	1.57
$C_{15}H_{30}N_2$	17.46	1.43
$C_{16}H_4NO_2$	18.11	1.75
$C_{16}H_6N_3$	18.48	1.61
$C_{16}H_{14}O_2$	17.58	1.85
$C_{16}H_{16}NO$	17.95	1.72
$C_{16}H_{18}N_2$	18.33	1.58
$C_{16}H_{30}O$	17.79	1.69
$C_{16}H_{32}N$	18.17	1.56
$C_{17}HO_2$	18.46	2.01
$C_{17}H_3NO$	18.84	1.88
$C_{17}H_5N_2$	19.21	1.75
$C_{17}H_{17}O$	18.68	1.85
$C_{17}H_{19}N$	19.06	1.72
$C_{17}H_{33}$	18.90	1.69
$C_{18}H_5O$	19.57	2.01
$C_{18}H_7N$	19.94	1.88
$C_{18}H_{21}$	19.79	1.85
$C_{19}H_9$	20.68	2.03
238		
$C_{11}H_4N_2O_4$	13.03	1.59
$C_{11}H_6N_3O_3$	13.40	1.43
$C_{11}H_8N_4O_2$	13.78	1.28
$C_{12}H_2N_2O_4$	13.92	1.70
$C_{12}H_4N_3O_3$	14.29	1.55
$C_{12}H_6N_4O_2$	14.67	1.40
$C_{12}H_{16}NO_4$	13.76	1.68
$C_{12}H_{18}N_2O_3$	14.14	1.53
$C_{12}H_{20}N_3O_2$	14.51	1.38
$C_{12}H_{22}N_4O$	14.88	1.24
$C_{13}H_6NO_4$	14.65	1.80
$C_{13}H_8N_2O_3$	15.02	1.65
$C_{13}H_{10}N_3O_2$	15.40	1.51
$C_{13}H_{12}N_4O$	15.77	1.37
$C_{13}H_{18}O_4$	14.49	1.78
$C_{13}H_{20}NO_3$	14.87	1.63
$C_{13}H_{22}N_2O_2$	15.24	1.49
$C_{13}H_{24}N_3O$	15.62	1.34
$C_{13}H_{26}N_4$	15.99	1.20
$C_{14}H_{10}O_4$	15.38	1.90
$C_{14}H_9NO_3$	15.76	1.76
$C_{14}H_{11}N_2O_2$	16.13	1.62
$C_{14}H_{13}N_3O$	16.50	1.48
$C_{14}H_{15}N_4$	16.88	1.34
$C_{14}H_{22}O_3$	15.60	1.74
$C_{14}H_{24}NO_2$	15.97	1.59
$C_{14}H_{26}N_2O$	16.35	1.45
$C_{14}H_{28}N_3$	16.72	1.31
$C_{15}H_2N_4$	17.77	1.49
$C_{15}H_{10}O_3$	16.49	1.87

	P + 1	P + 2
$C_{15}H_{12}NO_2$	16.86	1.73
$C_{15}H_{14}N_2O$	17.24	1.60
$C_{15}H_{16}N_2$	17.61	1.46
$C_{15}H_{18}O_2$	16.70	1.71
$C_{15}H_{19}NO$	17.08	1.57
$C_{15}H_{20}N_2$	17.45	1.43
$C_{16}H_9N_2O$	18.12	1.75
$C_{16}H_{11}N_3$	18.50	1.62
$C_{16}H_{14}O_2$	17.59	1.85
$C_{16}H_{15}NO$	17.97	1.72
$C_{16}H_{18}N_2$	18.34	1.59
$C_{16}H_{20}O$	17.81	1.69
$C_{16}H_{21}N$	18.18	1.56
$C_{17}H_7O_2$	18.48	2.01
$C_{17}H_8NO$	18.86	1.88
$C_{17}H_9N_2$	19.23	1.75
$C_{17}H_{18}O$	18.70	1.85
$C_{17}H_{19}N$	19.07	1.72
$C_{17}H_{34}$	18.91	1.69
$C_{18}H_6O$	19.59	2.01
$C_{18}H_7N$	19.96	1.89
$C_{18}H_{22}$	19.80	1.86
$C_{19}H_{10}$	20.69	2.03

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$C_{11}H_{15}N_2O_4$	13.05	1.59
$C_{11}H_{17}N_2O_3$	13.42	1.44
$C_{11}H_{18}N_4O_2$	13.80	1.29
$C_{12}H_2N_2O_4$	13.93	1.70
$C_{12}H_5N_3O_3$	14.31	1.55
$C_{12}H_7N_4O_2$	14.68	1.41
$C_{12}H_{17}NO_4$	13.78	1.68
$C_{12}H_{18}N_2O_3$	14.15	1.53
$C_{12}H_{21}N_3O_2$	14.53	1.38
$C_{12}H_{23}N_4O$	14.90	1.24
$C_{13}H_6NO_4$	14.67	1.80
$C_{13}H_7N_2O_3$	15.04	1.66
$C_{13}H_9N_3O_2$	15.41	1.51
$C_{13}H_{11}N_4O$	15.79	1.37
$C_{13}H_{19}O_4$	14.51	1.78
$C_{13}H_{21}NO_3$	14.88	1.63
$C_{13}H_{23}N_2O_2$	15.26	1.49
$C_{13}H_{25}N_3O$	15.63	1.34
$C_{14}H_{17}N_4$	16.01	1.20
$C_{14}H_7O_4$	15.40	1.91
$C_{14}H_8NO_3$	15.77	1.76
$C_{14}H_{11}N_2O_2$	16.15	1.62
$C_{14}H_{13}N_3O$	16.52	1.48
$C_{14}H_{15}N_4$	16.89	1.34
$C_{14}H_{23}O_3$	15.61	1.74
$C_{14}H_{25}NO_2$	15.99	1.60
$C_{14}H_{27}N_2O$	16.36	1.46
$C_{14}H_{29}N_3$	16.74	1.32
$C_{15}HN_3O$	17.41	1.63
$C_{15}H_5N_4$	17.78	1.49
$C_{15}H_{11}O_3$	16.50	1.88
$C_{15}H_{13}NO_2$	16.88	1.74
$C_{15}H_{15}N_2O$	17.25	1.60
$C_{15}H_{17}N_3$	17.63	1.46
$C_{15}H_{27}O_2$	16.72	1.71
$C_{15}H_{29}NO$	17.09	1.57
$C_{15}H_{31}N_2$	17.47	1.44
$C_{16}HNO_2$	17.77	1.88
$C_{16}H_3N_2O$	18.14	1.75
$C_{16}H_5N_3$	18.51	1.62
$C_{16}H_{13}O_2$	17.61	1.86
$C_{16}H_{13}NO$	17.98	1.72
$C_{16}H_{15}N_2$	18.36	1.59
$C_{16}H_{17}O$	17.83	1.70
$C_{16}H_{23}N$	18.20	1.56
$C_{17}H_3O_2$	18.50	2.01
$C_{17}H_5NO$	18.87	1.88
$C_{17}H_7N_2$	19.25	1.75
$C_{17}H_{19}O$	18.71	1.85
$C_{17}H_{21}N$	19.09	1.72
$C_{17}H_{35}$	18.93	1.69
$C_{18}H_7O$	19.60	2.02
$C_{18}H_9N$	19.98	1.89
$C_{18}H_{23}$	19.82	1.86
$C_{19}H_{11}$	20.71	2.03

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$C_{11}H_{16}N_2O_4$	13.06	1.59
$C_{11}H_{18}N_3O_3$	13.44	1.44
$C_{11}H_{20}N_4O_2$	13.81	1.29
$C_{12}H_4N_2O_4$	13.95	1.70
$C_{12}H_6N_3O_3$	14.33	1.56
$C_{12}H_8N_4O_2$	14.70	1.41
$C_{12}H_{18}NO_4$	13.79	1.68
$C_{12}H_{20}N_2O_3$	14.17	1.53
$C_{12}H_{22}N_3O_2$	14.54	1.39
$C_{12}H_{24}N_4O$	14.92	1.24
$C_{13}H_8NO_4$	14.68	1.80
$C_{13}H_9N_2O_3$	15.06	1.66
$C_{13}H_{10}N_3O_2$	15.43	1.51
$C_{13}H_{12}N_4O$	15.81	1.37
$C_{13}H_{20}O_4$	14.52	1.78
$C_{13}H_{22}NO_3$	14.90	1.63
$C_{13}H_{24}N_2O_2$	15.27	1.49
$C_{13}H_{26}N_3O$	15.65	1.35
$C_{14}H_{28}N_4$	16.02	1.20
$C_{14}H_8O_4$	15.41	1.91
$C_{14}H_9NO_3$	15.79	1.77
$C_{14}H_{12}N_2O_2$	16.16	1.62
$C_{14}H_{14}N_3O$	16.54	1.48
$C_{14}H_{16}N_4$	16.91	1.35
$C_{14}H_{24}O_3$	15.63	1.74
$C_{14}H_{26}NO_2$	16.00	1.60
$C_{14}H_{28}N_2O$	16.38	1.46
$C_{14}H_{30}N_3$	16.75	1.32
$C_{15}H_2N_3O$	17.42	1.63
$C_{15}H_4N_4$	17.80	1.49
$C_{15}H_{12}O_3$	16.52	1.88
$C_{15}H_{14}NO_2$	16.89	1.74
$C_{15}H_{16}N_2O$	17.27	1.60
$C_{15}H_{18}N_3$	17.64	1.47
$C_{15}H_{28}O_2$	16.74	1.71
$C_{15}H_{30}NO$	17.11	1.58
$C_{15}H_{32}N_2$	17.48	1.44
$C_{16}H_2NO_2$	17.78	1.89
$C_{16}H_4N_2O$	18.16	1.75
$C_{16}H_6N_3$	18.53	1.62
$C_{16}H_{16}O_2$	17.62	1.86
$C_{16}H_{18}NO$	18.00	1.73
$C_{16}H_{20}N_2$	18.37	1.59
$C_{16}H_{32}O$	17.84	1.70
$C_{16}H_{34}N$	18.22	1.56
$C_{17}H_4O_2$	18.51	2.02
$C_{17}H_6NO$	18.89	1.88
$C_{17}H_8N_2$	19.26	1.75
$C_{17}H_{20}O$	18.73	1.86
$C_{17}H_{22}N$	19.10	1.72
$C_{17}H_{36}$	18.95	1.70
$C_{18}H_8O$	19.62	2.02
$C_{18}H_{10}N$	19.99	1.89
$C_{18}H_{24}$	19.84	1.86
$C_{19}H_{12}$	20.72	2.04

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$C_{11}H_{17}N_2O_4$	13.08	1.59
$C_{11}H_{19}N_3O_3$	13.45	1.44
$C_{11}H_{21}N_4O_2$	13.83	1.29
$C_{12}H_3N_2O_4$	13.97	1.71
$C_{12}H_5N_3O_3$	14.34	1.56
$C_{12}H_9N_4O_2$	14.72	1.41
$C_{12}H_{19}NO_4$	13.81	1.68
$C_{12}H_{21}N_2O_3$	14.18	1.54
$C_{12}H_{23}N_3O_2$	14.56	1.39
$C_{12}H_{25}N_4O$	14.93	1.24
$C_{13}H_7NO_4$	14.70	1.81
$C_{13}H_8N_2O_3$	15.07	1.66
$C_{13}H_{11}N_3O_2$	15.45	1.52
$C_{13}H_{13}N_4O$	15.82	1.37
$C_{13}H_{21}O_4$	14.54	1.78
$C_{13}H_{23}NO_3$	14.92	1.64
$C_{13}H_{25}N_2O_2$	15.29	1.49
$C_{13}H_{27}N_3O$	15.66	1.35
$C_{14}H_{29}N_4$	16.04	1.21
$C_{14}H_9O_4$	16.71	1.51
$C_{14}H_{10}NO_3$	15.43	1.91
$C_{14}H_{11}NO_4$	15.80	1.77
$C_{14}H_{13}N_2O_2$	16.18	1.63
$C_{14}H_{15}N_3O$	16.55	1.49
$C_{14}H_{17}N_4$	16.93	1.35
$C_{14}H_{25}O_3$	15.65	1.74
$C_{14}H_{27}NO_2$	16.02	1.60
$C_{14}H_{29}N_2O$	16.39	1.46
$C_{14}H_{31}N_3$	16.77	1.32
$C_{15}HN_2O_2$	17.07	1.77
$C_{15}H_3N_3O$	17.44	1.63
$C_{15}H_5N_4$	17.82	1.50
$C_{15}H_{13}O_3$	16.53	1.88
$C_{15}H_{15}NO_2$	16.91	1.74
$C_{15}H_{17}N_2O$	17.28	1.60
$C_{15}H_{19}N_3$	17.66	1.47
$C_{15}H_{29}O_2$	16.75	1.72
$C_{15}H_{31}NO$	17.13	1.58
$C_{15}H_{33}N_2$	17.50	1.44
$C_{16}HO_3$	17.42	2.03
$C_{16}H_3NO_2$	17.80	1.89
$C_{16}H_5N_2O$	18.17	1.76
$C_{16}H_7N_3$	18.55	1.62
$C_{16}H_{17}O_2$	17.64	1.86
$C_{16}H_{19}NO$	18.01	1.73
$C_{16}H_{21}N_2$	18.39	1.60
$C_{16}H_{33}O$	17.86	1.70
$C_{16}H_{35}N$	18.23	1.57
$C_{17}H_5O_2$	18.53	2.02
$C_{17}H_7NO$	18.90	1.89
$C_{17}H_9N_2$	19.28	1.76
$C_{17}H_{21}O$	18.75	1.86
$C_{17}H_{23}N$	19.12	1.73
$C_{18}H_9O$	19.63	2.02
$C_{18}H_{11}N$	20.01	1.90
$C_{18}H_{25}$	19.85	1.87
$C_{19}H_{13}$	20.74	2.04
$C_{20}H$	21.63	2.22

242

$C_{11}H_{18}N_2O_4$	13.09	1.59
$C_{11}H_{20}N_3O_3$	13.47	1.44
$C_{11}H_{22}N_4O_2$	13.84	1.29
$C_{12}H_4N_2O_4$	13.98	1.71
$C_{12}H_6N_3O_3$	14.36	1.56
$C_{12}H_{10}N_4O_2$	14.73	1.41
$C_{12}H_{20}NO_4$	13.83	1.69
$C_{12}H_{22}N_2O_3$	14.20	1.54
$C_{12}H_{24}N_3O_2$	14.57	1.39
$C_{12}H_{26}N_4O$	14.95	1.24
$C_{13}H_8NO_4$	14.71	1.81
$C_{13}H_{10}N_2O_3$	15.09	1.66
$C_{13}H_{12}N_3O_2$	15.46	1.52
$C_{13}H_{14}N_4O$	15.84	1.38
$C_{13}H_{22}O_4$	14.56	1.79
$C_{13}H_{24}NO_3$	14.93	1.64
$C_{13}H_{26}N_2O_2$	15.31	1.49
$C_{13}H_{28}N_3O$	15.68	1.35
$C_{14}H_{30}N_4$	16.05	1.21
$C_{14}H_2N_4O$	16.73	1.51
$C_{14}H_{10}O_4$	15.45	1.91
$C_{14}H_{12}NO_3$	15.82	1.77
$C_{14}H_{14}N_2O_2$	16.19	1.63
$C_{14}H_{16}N_3O$	16.57	1.49
$C_{14}H_{18}N_4$	16.94	1.35
$C_{14}H_{26}O_3$	15.66	1.75
$C_{14}H_{28}NO_2$	16.04	1.60
$C_{14}H_{30}N_2O$	16.41	1.46
$C_{14}H_{32}N_3$	16.79	1.32
$C_{15}H_2N_2O_2$	17.08	1.77
$C_{15}H_4N_3O$	17.46	1.63
$C_{15}H_6N_4$	17.83	1.50
$C_{15}H_{14}O_3$	16.55	1.88
$C_{15}H_{16}NO_2$	16.93	1.74
$C_{15}H_{18}N_2O$	17.30	1.61
$C_{15}H_{20}N_3$	17.67	1.47
$C_{15}H_{30}O_2$	16.77	1.72
$C_{15}H_{32}NO$	17.14	1.58
$C_{15}H_{34}N_2$	17.52	1.45
$C_{16}H_2O_3$	17.44	2.03
$C_{16}H_4NO_2$	17.81	1.89
$C_{16}H_6N_2O$	18.19	1.76
$C_{16}H_8N_3$	18.56	1.63
$C_{16}H_{18}O_2$	17.66	1.87
$C_{16}H_{20}NO$	18.03	1.73
$C_{16}H_{22}N_2$	18.41	1.60
$C_{16}H_{34}O$	17.87	1.70
$C_{17}H_6O_2$	18.54	2.02
$C_{17}H_8NO$	18.92	1.89
$C_{17}H_{10}N_2$	19.29	1.76
$C_{17}H_{22}O$	18.76	1.86
$C_{17}H_{24}N$	19.14	1.73
$C_{18}H_{10}O$	19.65	2.03
$C_{18}H_{12}N$	20.02	1.90

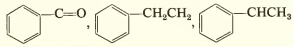
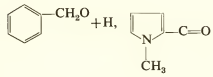
	P + 1	P + 2
$C_{18}H_{26}$	19.87	1.87
$C_{19}H_{14}$	20.76	2.04
$C_{20}H_2$	21.64	2.23
243		
$C_{11}H_{19}N_2O_4$	13.11	1.60
$C_{11}H_{21}N_2O_3$	13.48	1.44
$C_{11}H_{23}N_4O_2$	13.86	1.29
$C_{12}H_7N_2O_4$	14.00	1.71
$C_{12}H_9N_3O_3$	14.37	1.56
$C_{12}H_{11}N_4O_2$	14.75	1.42
$C_{12}H_{21}NO_4$	13.84	1.69
$C_{12}H_{23}N_2O_3$	14.22	1.54
$C_{12}H_{25}N_3O_2$	14.59	1.39
$C_{12}H_{27}N_4O$	14.96	1.25
$C_{13}H_9NO_4$	14.73	1.81
$C_{13}H_{11}N_2O_3$	15.10	1.66
$C_{13}H_{13}N_3O_2$	15.48	1.52
$C_{13}H_{15}N_4O$	15.85	1.38
$C_{13}H_{23}O_4$	14.57	1.79
$C_{13}H_{25}NO_3$	14.95	1.64
$C_{13}H_{27}N_2O_2$	15.32	1.50
$C_{13}H_{29}N_3O$	15.70	1.35
$C_{14}H_{21}N_4$	16.07	1.21
$C_{14}HN_3O_4$	16.37	1.66
$C_{14}H_3N_4O$	16.74	1.52
$C_{14}H_{11}O_4$	15.46	1.92
$C_{14}H_{13}NO_3$	15.84	1.77
$C_{14}H_{15}N_2O_2$	16.21	1.63
$C_{14}H_{17}N_3O$	16.58	1.49
$C_{14}H_{19}N_4$	16.96	1.35
$C_{14}H_{27}O_3$	15.68	1.75
$C_{14}H_{29}NO_2$	16.05	1.61
$C_{14}H_{31}N_2O$	16.43	1.47
$C_{14}H_{33}N_3$	16.80	1.33
$C_{15}HNO_3$	16.72	1.91
$C_{15}H_3N_2O_2$	17.10	1.77
$C_{15}H_5N_3O$	17.47	1.64
$C_{15}H_7N_4$	17.85	1.50
$C_{15}H_{15}O_3$	16.57	1.89
$C_{15}H_{17}NO_2$	16.94	1.75
$C_{15}H_{19}N_2O$	17.32	1.61
$C_{15}H_{21}N_3$	17.69	1.47
$C_{15}H_{31}O_2$	16.78	1.72
$C_{15}H_{33}NO$	17.16	1.58
$C_{16}H_9O_2$	17.46	2.03
$C_{16}H_{11}NO_2$	17.83	1.90
$C_{16}H_{13}N_2O$	18.20	1.76
$C_{16}H_{15}N_3$	18.58	1.63
$C_{16}H_{19}O_2$	17.67	1.87
$C_{16}H_{21}NO$	18.05	1.73
$C_{16}H_{23}N_2$	18.42	1.60
$C_{17}H_7O_2$	18.56	2.02
$C_{17}H_9NO$	18.94	1.89
$C_{17}H_{11}N_2$	19.31	1.76
$C_{17}H_{23}O$	18.78	1.86
$C_{17}H_{25}N$	19.15	1.73
$C_{18}H_{11}O$	19.67	2.03
$C_{18}H_{13}N$	20.04	1.90
$C_{18}H_{27}$	19.88	1.87
$C_{19}HN$	20.93	2.08
$C_{19}H_{15}$	20.77	2.05
$C_{20}H_3$	21.66	2.23
244		
$C_{11}H_{20}N_2O_4$	13.13	1.60
$C_{11}H_{22}N_2O_3$	13.50	1.45
$C_{11}H_{24}N_4O_2$	13.88	1.30
$C_{12}H_8NO_4$	14.01	1.71
$C_{12}H_{10}N_2O_3$	14.39	1.56
$C_{12}H_{12}N_4O_2$	14.76	1.42
$C_{12}H_{22}NO_4$	13.86	1.69
$C_{12}H_{24}N_2O_3$	14.23	1.54
$C_{12}H_{26}N_3O_2$	14.61	1.40
$C_{12}H_{28}N_4O$	14.98	1.25
$C_{13}H_{16}NO_4$	14.75	1.81
$C_{13}H_{12}N_2O_3$	15.12	1.67
$C_{13}H_{14}N_3O_2$	15.49	1.52
$C_{13}H_{16}N_4O$	15.87	1.38
$C_{13}H_{24}O_4$	14.59	1.79
$C_{13}H_{26}NO_3$	14.96	1.64
$C_{13}H_{28}N_2O_2$	15.34	1.50
$C_{13}H_{30}N_3O$	15.71	1.36
$C_{13}H_{32}N_4$	16.09	1.21
$C_{14}H_2N_2O_2$	16.38	1.66
$C_{14}H_4N_4O$	16.76	1.52
$C_{14}H_{12}O_4$	15.48	1.92
$C_{14}H_{14}NO_3$	15.85	1.78
$C_{14}H_{16}N_2O_2$	16.23	1.63
$C_{14}H_{18}N_3O$	16.60	1.49
$C_{14}H_{20}N_4$	16.97	1.36
$C_{14}H_{28}O_3$	15.69	1.75
$C_{14}H_{30}NO_2$	16.07	1.61
$C_{14}H_{32}N_2O$	16.44	1.47
$C_{15}H_2NO_3$	16.74	1.91
$C_{15}H_4N_2O_2$	17.11	1.78
$C_{15}H_6N_3O$	17.49	1.64
$C_{15}H_8N_4$	17.86	1.50
$C_{15}H_{16}O_3$	16.58	1.89
$C_{15}H_{18}NO_2$	16.96	1.75
$C_{15}H_{20}N_2O$	17.33	1.61
$C_{15}H_{22}N_3$	17.71	1.48
$C_{15}H_{32}O_2$	16.80	1.72
$C_{16}H_4O_3$	17.47	2.03
$C_{16}H_6NO_2$	17.85	1.90
$C_{16}H_8N_2O$	18.22	1.77
$C_{16}H_{10}N_3$	18.59	1.63
$C_{16}H_{20}O_2$	17.69	1.87
$C_{16}H_{22}NO$	18.06	1.74
$C_{16}H_{24}N_2$	18.44	1.60
$C_{17}H_8O_2$	18.58	2.03
$C_{17}H_{10}NO$	18.95	1.90
$C_{17}H_{12}N_2$	19.33	1.77
$C_{17}H_{24}O$	18.79	1.87
$C_{17}H_{26}N$	19.17	1.74
$C_{18}H_{12}O$	19.68	2.03
$C_{18}H_{14}N$	20.06	1.91
$C_{18}H_{28}$	19.90	1.87
$C_{19}H_2N$	20.95	2.08
$C_{19}H_{16}$	20.79	2.05
$C_{20}H_4$	21.68	2.23
245		
$C_{11}H_{21}N_2O_4$	13.14	1.60
$C_{11}H_{23}N_2O_3$	13.52	1.45
$C_{11}H_{25}N_4O_2$	13.89	1.30
$C_{12}H_9N_2O_4$	14.03	1.71
$C_{12}H_{11}N_3O_3$	14.41	1.57
$C_{12}H_{13}N_4O_2$	14.78	1.42
$C_{12}H_{23}NO_4$	13.87	1.69
$C_{12}H_{25}N_2O_3$	14.25	1.54
$C_{12}H_{27}N_3O_2$	14.62	1.40
$C_{12}H_{29}N_4O$	15.00	1.25
$C_{13}HNO_4$	15.67	1.55
$C_{13}H_3N_2O_3$	14.76	1.81
$C_{13}H_5N_3O_2$	15.14	1.67
$C_{13}H_7N_4O_2$	15.51	1.53
$C_{13}H_{17}N_4O$	15.89	1.38
$C_{13}H_{25}O_4$	14.60	1.79
$C_{13}H_{27}NO_3$	14.98	1.65
$C_{13}H_{29}N_2O_2$	15.35	1.50
$C_{13}H_{31}N_3O$	15.73	1.36
$C_{14}HN_2O_3$	16.03	1.80
$C_{14}H_3N_3O_2$	16.40	1.66
$C_{14}H_5N_4O$	16.77	1.52
$C_{14}H_{13}O_4$	15.49	1.92
$C_{14}H_{15}NO_3$	15.87	1.78
$C_{14}H_{17}N_2O_2$	16.24	1.64
$C_{14}H_{19}N_3O$	16.62	1.50
$C_{14}H_{21}N_4$	16.99	1.36
$C_{14}H_{29}O_3$	15.71	1.75
$C_{14}H_{31}NO_2$	16.08	1.61
$C_{15}HO_4$	16.38	2.06
$C_{15}H_3NO_3$	16.76	1.92
$C_{15}H_5N_2O_2$	17.13	1.78
$C_{15}H_7N_3O$	17.50	1.64
$C_{15}H_9N_4$	17.88	1.51
$C_{15}H_{17}O_3$	16.60	1.89
$C_{15}H_{19}NO_2$	16.97	1.75
$C_{15}H_{21}N_2O$	17.35	1.62
$C_{15}H_{23}N_3$	17.72	1.48
$C_{16}H_5O_3$	17.49	2.04
$C_{16}H_7NO_2$	17.86	1.90
$C_{16}H_9N_2O$	18.24	1.77
$C_{16}H_{11}N_3$	18.61	1.64
$C_{16}H_{21}O_2$	17.70	1.87
$C_{16}H_{23}NO$	18.08	1.74
$C_{16}H_{25}N_2$	18.45	1.61
$C_{17}H_9O_2$	18.59	2.03
$C_{17}H_{11}NO$	18.97	1.90
$C_{17}H_{13}N_2$	19.34	1.77
$C_{17}H_{25}O$	18.81	1.87
$C_{17}H_{27}N$	19.18	1.74
$C_{18}HN_2$	20.23	1.94
$C_{18}H_{13}O$	19.70	2.04
$C_{18}H_{15}N$	20.07	1.91
$C_{18}H_{29}$	19.92	1.88
$C_{19}H_{17}$	20.80	2.05
$C_{19}HO$	20.59	2.21
$C_{19}H_2N$	20.96	2.09
$C_{20}H_6$	21.69	2.24
246		
$C_{11}H_{22}N_2O_4$	13.16	1.60
$C_{11}H_{24}N_2O_3$	13.53	1.45
$C_{11}H_{26}N_4O_2$	13.91	1.30
$C_{12}H_{10}N_2O_4$	14.05	1.72
$C_{12}H_{12}N_3O_3$	14.42	1.57
$C_{12}H_{14}N_4O_2$	14.80	1.42
$C_{12}H_{24}NO_4$	13.89	1.70
$C_{12}H_{26}N_2O_3$	14.26	1.55
$C_{12}H_{28}N_3O_2$	14.64	1.40
$C_{12}H_{30}N_4O$	15.01	1.25
$C_{13}H_2N_4O_2$	15.68	1.55
$C_{13}H_{12}NO_4$	14.78	1.82
$C_{13}H_{14}N_2O_3$	15.15	1.67
$C_{13}H_{16}N_3O_2$	15.53	1.53
$C_{13}H_{18}N_4O$	15.90	1.39
$C_{13}H_{26}O_4$	14.62	1.79
$C_{13}H_{28}NO_3$	15.00	1.65
$C_{13}H_{30}N_2O_2$	15.37	1.50
$C_{14}H_2N_2O_3$	16.04	1.80
$C_{14}H_4N_3O_2$	16.42	1.66
$C_{14}H_6N_4O$	16.79	1.53
$C_{14}H_{14}O_4$	15.51	1.92
$C_{14}H_{16}NO_3$	15.88	1.78
$C_{14}H_{18}N_2O_2$	16.26	1.64
$C_{14}H_{20}N_3O$	16.63	1.50
$C_{14}H_{22}N_4$	17.01	1.36
$C_{14}H_{30}O_3$	15.73	1.76
$C_{15}H_2O_4$	16.40	2.06
$C_{15}H_4NO_3$	16.77	1.92
$C_{15}H_6N_2O_2$	17.15	1.78
$C_{15}H_8N_3O$	17.52	1.65
$C_{15}H_{10}N_4$	17.90	1.51
$C_{15}H_{18}O_3$	16.61	1.89
$C_{15}H_{20}NO_2$	16.99	1.76
$C_{15}H_{22}N_2O$	17.36	1.62
$C_{15}H_{24}N_3$	17.74	1.48
$C_{16}H_6O_3$	17.50	2.04
$C_{16}H_8NO_2$	17.88	1.90
$C_{16}H_{10}N_2O$	18.25	1.77
$C_{16}H_{12}N_3$	18.63	1.64
$C_{16}H_{22}O_2$	17.72	1.88
$C_{16}H_{24}NO$	18.09	1.74
$C_{16}H_{26}N_2$	18.47	1.61
$C_{17}H_{10}O_2$	18.61	2.03
$C_{17}H_{12}NO$	18.98	1.90
$C_{17}H_{14}N_2$	19.36	1.77
$C_{17}H_{26}O$	18.83	1.87
$C_{17}H_{28}N$	19.20	1.74
$C_{18}H_2N_2$	20.25	1.94
$C_{18}H_{14}O$	19.71	2.04
$C_{18}H_{16}N$	20.09	1.91
$C_{18}H_{30}$	19.93	1.88
$C_{19}H_2O$	20.60	2.21
$C_{19}H_4N$	20.98	2.09
$C_{19}H_{18}$	20.82	2.06
$C_{20}H_8$	21.71	2.24
247		
$C_{11}H_{23}N_2O_4$	13.17	1.60
$C_{11}H_{25}N_2O_3$	13.55	1.45
$C_{11}H_{27}N_4O_2$	13.92	1.30
$C_{12}H_{11}N_2O_4$	14.06	1.72
$C_{12}H_{13}N_3O_3$	14.44	1.57
$C_{12}H_{15}N_4O_2$	14.81	1.42
$C_{12}H_{25}NO_4$	13.91	1.70
$C_{12}H_{27}N_2O_3$	14.28	1.55
$C_{12}H_{29}N_3O_2$	14.65	1.40
$C_{13}HN_3O_3$	15.33	1.70
$C_{13}H_3N_4O_2$	15.70	1.55
$C_{13}H_{13}NO_4$	14.79	1.82
$C_{13}H_{15}N_2O_3$	15.17	1.67

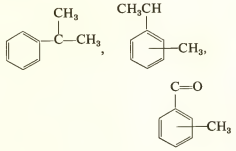
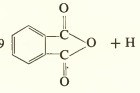
	P + 1	P + 2
$C_{12}H_{17}N_3O_2$	15.54	1.53
$C_{13}H_{19}N_4O$	15.92	1.39
$C_{13}H_{27}O_4$	14.64	1.80
$C_{13}H_{29}NO_3$	15.01	1.65
$C_{14}HNO_4$	15.68	1.95
$C_{14}H_5N_3O_3$	16.06	1.81
$C_{14}H_9N_3O_2$	16.43	1.67
$C_{14}H_7N_4O$	16.81	1.53
$C_{14}H_{15}O_4$	15.53	1.93
$C_{14}H_{17}NO_3$	15.90	1.78
$C_{14}H_{19}N_2O_2$	16.27	1.64
$C_{14}H_{21}N_2O$	16.65	1.50
$C_{14}H_{23}N_4$	17.02	1.36
$C_{15}H_3O_4$	16.41	2.06
$C_{15}H_5NO_3$	16.79	1.92
$C_{15}H_7N_2O_2$	17.16	1.78
$C_{15}H_9N_3O$	17.54	1.65
$C_{15}H_{11}N_4$	17.91	1.51
$C_{15}H_{19}O_3$	16.63	1.90
$C_{15}H_{21}NO_2$	17.01	1.76
$C_{15}H_{23}N_2O$	17.38	1.62
$C_{15}H_{25}N_3$	17.75	1.49
$C_{16}H_7O_3$	17.52	2.04
$C_{16}H_9NO_2$	17.89	1.91
$C_{16}H_{11}N_2O$	18.27	1.77
$C_{16}H_{13}N_3$	18.64	1.64
$C_{16}H_{25}O_3$	17.74	1.88
$C_{16}H_{27}NO$	18.11	1.75
$C_{16}H_{27}N_2$	18.49	1.61
$C_{17}HN_3$	19.53	1.81
$C_{17}H_{11}O_2$	18.62	2.04
$C_{17}H_{13}NO$	19.00	1.91
$C_{17}H_{15}N_2$	19.37	1.78
$C_{17}H_{27}O$	18.84	1.88
$C_{17}H_{29}N$	19.22	1.75
$C_{18}HNO$	19.89	2.07
$C_{18}H_3N_2$	20.26	1.95
$C_{18}H_{15}O$	19.73	2.04
$C_{18}H_{17}N$	20.10	1.92
$C_{18}H_{31}$	19.95	1.88
$C_{19}H_3O$	20.62	2.22
$C_{19}H_5N$	20.99	2.09
$C_{19}H_{19}$	20.84	2.06
$C_{20}H_7$	21.72	2.24
248		
$C_{11}H_{24}N_2O_4$	13.19	1.61
$C_{11}H_{28}N_4O_3$	13.56	1.45
$C_{11}H_{29}N_4O_2$	13.94	1.31
$C_{12}H_{12}N_2O_4$	14.08	1.72
$C_{12}H_{14}N_4O_3$	14.45	1.57
$C_{12}H_{16}N_4O_2$	14.83	1.43
$C_{12}H_{28}NO_4$	13.92	1.70
$C_{12}H_{32}N_2O_3$	14.30	1.55
$C_{13}H_8N_2O_3$	15.34	1.70
$C_{13}H_{10}N_4O$	15.72	1.56
$C_{13}H_{14}NO_4$	14.81	1.82
$C_{13}H_{16}N_2O_3$	15.18	1.68
$C_{13}H_{18}N_3O_2$	15.56	1.53
$C_{13}H_{20}N_4O$	15.93	1.39
$C_{13}H_{28}O_4$	14.65	1.80
$C_{14}H_2NO_4$	15.70	1.95
$C_{14}H_4N_2O_3$	16.07	1.81
$C_{14}H_6N_3O_2$	16.45	1.67
$C_{14}H_8N_4O$	16.82	1.53
$C_{14}H_{16}O_4$	15.54	1.93
$C_{14}H_{18}NO_3$	15.92	1.79
$C_{14}H_{20}N_2O_2$	16.29	1.64
$C_{14}H_{22}N_3O$	16.66	1.51
$C_{14}H_{24}N_4$	17.04	1.37
$C_{15}H_4O_4$	16.43	2.06
$C_{15}H_6NO_3$	16.80	1.92
$C_{15}H_8N_2O_2$	17.18	1.79
$C_{15}H_{10}N_3O$	17.55	1.65
$C_{15}H_{12}N_4$	17.93	1.52
$C_{15}H_{20}O_3$	16.65	1.90
$C_{15}H_{22}NO_2$	17.02	1.76
$C_{15}H_{24}N_2O$	17.40	1.62
$C_{15}H_{26}N_3$	17.77	1.49
$C_{16}H_8O_3$	17.54	2.05
$C_{16}H_{10}NO_2$	17.91	1.91
$C_{16}H_{12}N_2O$	18.28	1.78
$C_{16}H_{14}N_3$	18.66	1.65
$C_{16}H_{26}O_3$	17.75	1.88
$C_{16}H_{26}NO$	18.13	1.75
$C_{16}H_{28}N_2$	18.50	1.62
$C_{17}H_2N_3$	19.55	1.81
$C_{17}H_{12}O_2$	18.64	2.04
$C_{17}H_{14}NO$	19.02	1.91
$C_{17}H_{16}N_2$	19.39	1.78
$C_{17}H_{28}O$	18.86	1.88
$C_{17}H_{30}N$	19.23	1.75
$C_{18}H_2NO$	19.90	2.08
$C_{18}H_4N_2$	20.28	1.95
$C_{18}H_{16}O$	19.75	2.04
$C_{18}H_{18}N$	20.12	1.92
$C_{18}H_{32}$	19.96	1.89
$C_{19}H_4O$	20.64	2.22
$C_{19}H_6N$	21.01	2.10
$C_{19}H_{20}$	20.85	2.06
$C_{20}H_8$	21.74	2.25
249		
$C_{11}H_{23}N_2O_4$	13.21	1.61
$C_{11}H_{27}N_4O_3$	13.58	1.46
$C_{12}H_{13}N_2O_4$	14.10	1.72
$C_{12}H_{15}N_4O_3$	14.47	1.58
$C_{12}H_{17}N_4O_2$	14.84	1.43
$C_{12}H_{17}NO_4$	13.94	1.70
$C_{13}H_{19}N_4O$	14.98	1.85
$C_{13}H_{21}N_2O_3$	15.36	1.70
$C_{13}H_{23}N_4O_2$	15.73	1.56
$C_{13}H_{15}NO_4$	14.83	1.82
$C_{13}H_{17}N_2O_3$	15.20	1.68
$C_{13}H_{19}N_3O_2$	15.57	1.54
$C_{13}H_{21}N_4O$	15.95	1.39
$C_{14}H_9NO_4$	15.71	1.95
$C_{14}H_{11}N_2O_3$	16.09	1.81
$C_{14}H_{13}N_3O_2$	16.46	1.67
$C_{14}H_{15}N_4O$	16.84	1.53
$C_{14}H_{17}O_4$	15.56	1.93
$C_{14}H_{19}NO_3$	15.93	1.79
$C_{14}H_{21}N_2O_2$	16.31	1.65
$C_{14}H_{23}N_3O$	16.68	1.51
$C_{14}H_{25}N_4$	17.05	1.37
$C_{15}H_5O_4$	16.45	2.07
$C_{15}H_7NO_3$	16.82	1.93
$C_{15}H_9N_2O_2$	17.19	1.79
$C_{15}H_{11}N_3O$	17.57	1.65
$C_{15}H_{13}N_4$	17.94	1.52
$C_{15}H_{21}O_3$	16.66	1.90
$C_{15}H_{23}NO_2$	17.04	1.76
$C_{15}H_{25}N_2O$	17.41	1.63
$C_{15}H_{27}N_3$	17.79	1.49
$C_{16}HN_4$	18.83	1.68
$C_{16}H_9N_3$	17.55	2.05
$C_{16}H_{11}NO_2$	17.93	1.91
$C_{16}H_{13}N_2O$	18.30	1.78
$C_{16}H_{15}N_3$	18.67	1.65
$C_{16}H_{25}O_2$	17.77	1.89
$C_{16}H_{27}NO$	18.14	1.75
$C_{16}H_{29}N_2$	18.52	1.62
$C_{17}HN_2O$	19.19	1.94
$C_{17}H_3N_2$	19.56	1.81
$C_{17}H_{13}O_2$	18.66	2.04
$C_{17}H_{15}NO$	19.03	1.91
$C_{17}H_{17}N_2$	19.41	1.78
$C_{17}H_{29}O$	18.87	1.88
$C_{17}H_{31}N$	19.25	1.75
$C_{18}HO_2$	19.55	2.21
$C_{18}H_3NO$	19.92	2.08
$C_{18}H_5N_2$	20.29	1.95
$C_{18}H_{17}O$	19.76	2.05
$C_{18}H_{19}N$	20.14	1.92
$C_{18}H_{33}$	19.98	1.89
$C_{19}H_5O$	20.65	2.22
$C_{19}H_7N$	21.03	2.10
$C_{19}H_{21}$	20.87	2.07
$C_{20}H_9$	21.76	2.25
250		
$C_{11}H_{26}N_2O_4$	13.22	1.61
$C_{12}H_{14}N_2O_4$	14.11	1.73
$C_{12}H_{16}N_4O_3$	14.49	1.58
$C_{12}H_{18}N_4O_2$	14.86	1.43
$C_{12}H_2NO_4$	15.00	1.85
$C_{13}H_4N_2O_3$	15.37	1.71
$C_{13}H_6N_4O_2$	15.75	1.56
$C_{13}H_{16}NO_4$	14.84	1.83
$C_{13}H_{18}N_2O_3$	15.22	1.68
$C_{13}H_{20}N_3O_2$	15.59	1.54
$C_{13}H_{22}N_4O$	15.97	1.40
$C_{14}H_4NO_4$	15.73	1.96
$C_{14}H_6N_2O_3$	16.11	1.82
$C_{14}H_8N_3O_2$	16.48	1.67
$C_{14}H_{10}N_4O$	16.85	1.54
$C_{14}H_{18}O_4$	15.57	1.93
$C_{14}H_{20}NO_3$	15.95	1.79
$C_{14}H_{22}N_2O_2$	16.32	1.65
$C_{14}H_{24}N_3O$	16.70	1.51
$C_{14}H_{26}N_4$	17.07	1.37
$C_{15}H_6O_4$	16.46	2.07
$C_{15}H_8NO_3$	16.84	1.93
$C_{15}H_{10}N_2O_2$	17.21	1.79
$C_{15}H_{12}N_3O$	17.58	1.66
$C_{15}H_{14}N_4$	17.96	1.52
$C_{15}H_{22}O_3$	16.68	1.90
$C_{15}H_{24}NO_2$	17.05	1.77
$C_{15}H_{26}N_2O$	17.43	1.63
$C_{15}H_{28}N_3$	17.80	1.49
$C_{16}H_2N_4$	18.85	1.68
$C_{16}H_{10}O_3$	17.57	2.05
$C_{16}H_{12}NO_2$	17.94	1.92
$C_{16}H_{14}N_2O$	18.32	1.78
$C_{16}H_{16}N_3$	18.69	1.65
$C_{16}H_{26}O_2$	17.78	1.89
$C_{16}H_{28}NO$	18.16	1.75
$C_{16}H_{30}N_2$	18.53	1.62
$C_{17}H_2N_2O$	19.20	1.94
$C_{17}H_4N_3$	19.58	1.82
$C_{17}H_{14}O_2$	18.67	2.05
$C_{17}H_{16}NO$	19.05	1.91
$C_{17}H_{18}N_2$	19.42	1.79
$C_{17}H_{30}O$	18.89	1.89
$C_{17}H_{32}N$	19.26	1.76
$C_{18}H_2O_2$	19.56	2.21
$C_{18}H_4NO$	19.94	2.08
$C_{18}H_6N_2$	20.31	1.96
$C_{18}H_{18}O$	19.78	2.05
$C_{18}H_{20}N$	20.15	1.92
$C_{18}H_{34}$	20.00	1.89
$C_{19}H_6O$	20.67	2.23
$C_{19}H_8N$	21.04	2.10
$C_{19}H_{22}$	20.88	2.07
$C_{20}H_{10}$	21.77	2.25

APPENDIX B Common Fragments

m/e	Fragments
14	CH_2
15	CH_3
16	O
17	OH
18	H_2O, NH_4
19	F
20	HF
26	$C{\equiv}N$
27	C_2H_3
28	C_2H_4, CO, N_2
29	C_2H_5, CHO
30	CH_2NH_2, NO
31	CH_2OH, OCH_3
33	SH
34	H_2S
35	Cl
36	HCl
39	C_3H_3
40	$CH_2C{\equiv}N$
41	C_3H_5, $CH_2C{\equiv}N + H$
42	C_3H_6
43	C_3H_7, $CH_3C{=}O$
44	$H_2C{=}O + H$, CH_3CHNH_2, CO_2
45	$CHOH$, CH_2CH_2OH, CH_2OCH_3, $CH_3CH{-}O + H$
46	NO_2
47	CH_2SH, CH_3S
48	$CH_3S + H$
54	$CH_2CH_2C{\equiv}N$
55	C_4H_7
56	C_4H_8
57	C_4H_9, $C_2H_5C{=}O$
58	$CH_3{-}C(=O){-}CH_2 + H$, $C_2H_5CHNH_2$, $(CH_3)_2NCH_2$, $C_2H_5NHCH_2$
59	$(CH_3)_2COH$, $CH_2OC_2H_5$, $NH_2C{=}O + H$
60	$CH_2C(=O)OH + H$, CH_2ONO
61	$C{-}OCH_3 + 2H$, CH_2CH_2SH, CH_2SCH_3
68	$CH_2CH_2CH_2C{\equiv}N$
69	C_5H_9, CF_3
70	C_5H_{10}
71	C_5H_{11}, $C_3H_7C{=}O$

m/e	Fragments
72	$C_2H_5C(=O)CH_2 + H$, $C_3H_7CHNH_2$
73	$C{-}OC_2H_5$
74	$CH_2{-}C(=O){-}OCH_3 + H$
75	$C{-}OC_2H_5 + 2H$, $CH_2SC_2H_5$
77	C_6H_5
78	$C_6H_5 + H$
79	$C_6H_5 + 2H$, Br
80	 CH_2, $CH_3SS + H$, HBr
81	 CH_2
82	$CH_3CH_2CH_2CH_2C{\equiv}N$
83	C_6H_{11}
85	C_6H_{13}, $C_4H_9C{=}O$
86	$C_3H_7C(=O)CH_2 + H$, $C_4H_9CHNH_2$
87	$C{-}OC_3H_7$
88	$CH_2{-}C(=O){-}OC_3H_5 + H$
89	$C{-}OC_3H_7 + 2H$, C
90	CH_3CHONO_2,  CH
91	 CH_2, CH + H, C + 2H
92	 CH_2 + H, CH_2
94	 O + H,  C=O

m/e	Fragments
95	
96	$CH_2CH_2CH_2CH_2CH_2C{\equiv}N$
97	C_7H_{13}, 
98	 $+ H$
99	C_7H_{15}
100	$C_4H_9C(=O)CH_2 + H$, $C_5H_{11}CHNH_2$
101	$C(=O)OC_4H_9$
102	$CH_2C(=O)OC_3H_7 + H$
103	$C(=O)OC_4H_9 + 2H$
104	$C_2H_5CHONO_2$
105	
107	
108	

m/e	Fragments
111	
119	CF_3CF_2, 
121	
123	
127	I
128	HI
131	C_3F_5
139	
149	

CHAPTER THREE

Infrared Spectrometry

INTRODUCTION

Infrared radiation refers broadly to that part of the electromagnetic spectrum of longer wavelength than the visible region and shorter wavelength than the microwave region. Of greatest practical use to the organic chemist is the very limited portion of infrared radiation between about 4000 cm^{-1} and 660 cm^{-1} (2.5 μ and 15 μ). Radiation energy in this region is absorbed by the organic molecule and converted into energy of molecular vibration. The energy absorption pattern thus obtained is commonly referred to by the organic chemist as an infrared spectrum. In its usual form, it is a plot of intensities (either as percent transmittance or as absorbance) versus wavelength (microns) or frequency (wavenumbers) of absorption.

As with the other forms of energy probes covered in this book, the organic chemist has learned to interpret infrared spectra on an empirical basis. In the brief theoretical discussion that follows, it is clear that even a fairly simple molecule can give an extremely complex pattern. The organic chemist takes advantage of this complexity when he matches a spectrum of an unknown compound against that of an authentic sample. A peak-by-peak correlation is excellent evidence for identity. On the other hand, it turns out that certain groups of

atoms give rise to vibration bands at or near the same frequency regardless of the structure of the rest of the molecule. It is this feature which permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies.

We shall rely heavily on these characteristic group frequencies. Since we do not rely solely on infrared spectra for identification, a detailed analysis of the spectrum is not required.

Following our general plan, we shall present only sufficient theory to accomplish our purpose—utilization of infrared spectra in conjunction with our other spectral data in the determination of molecular structure. We shall describe instrumentation and operation in somewhat more detail than was given in the chapters on mass spectrometry and NMR spectrometry. In contrast with the instruments required to obtain NMR and mass spectra, an infrared spectrophotometer is frequently used by the organic chemist as a bench tool to follow reactions and work-ups. A simplified instrument costs about $5000. Precision spectrophotometers are available at $12,000 to $15,000 from a number of manufacturers.

There is no lack of reference material covering all aspects of infrared spectrometry.[1–10] The "bible" for empirical interpretation of infrared spectra is Bellamy's text.[3] Cross's compact manual[4] is an extremely convenient source of concise information. There are seven principal compilations of infrared spectra.[8,11–16] The annual reviews on infrared spectrometry which appear in *Analytical Chemistry*, are an excellent source for current information.

THEORY

Infrared radiation of wavelengths longer than about 100 μ is absorbed and converted by an organic molecule into energy of molecular rotation. This absorption is quantized; thus, a molecular rotation spectrum consists of discrete lines.

Infrared radiation in the range from about 1 to 100 μ is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized, but vibrational spectra appear as bands rather than lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with these vibrational bands—particularly those occurring between 2.5 and 15 μ—that we shall be concerned.

Band positions in infrared spectra are presented either as wavelengths or frequencies. The common unit of wavelength in infrared spectrometry is the micron (μ), equal to 10^{-3} mm. Frequencies are usually expressed in terms of wavenumbers ($\bar{\nu}$) whose unit is the reciprocal centimeter (cm^{-1}). In terms of this unit, the wavenumber is the reciprocal of the wavelength in centimeters. Or, when the wavelength is in microns, the wavenumber is $\frac{1}{\mu} \times 10^4$.

Band intensities are expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance, $A = \log_{10}(1/T)$. A concise compilation of approved spectrometry nomenclature has recently been published.[17]

There are two types of molecular vibrations: stretching and bending. A stretching vibration is a vibration along the bond axis such that the distance between the two atoms is increased or decreased. A bending vibration involves a change in bond angles. Only those stretching and bending vibrations which result in a rythmical change in the dipole moment of the molecule are observed in the infrared. It is the net change in charge distribution within the molecule produced by stretching and bending which makes interaction possible between the molecule and the oscillating field of the infrared radiation. The various stretching and bending modes for an AX_2 group are shown in Figure 1.

A nonlinear molecule of n atoms has $3n - 6$ possible fundamental vibrations. The theoretical number of fundamental vibrations (absorption frequencies) will not be observed because overtones and combination tones can increase, and other phenomena can reduce, the number of observed bands. The following can reduce the theoretical number of bands.

1. Fundamental frequencies which fall outside of the 2.5 – 15 μ region.
2. Fundamental bands which are too weak to be observed.
3. Fundamental vibrations which are so close that the bands coalesce.
4. The occurrence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.
5. The failure of certain fundamental vibrations to appear in the infrared because of lack of required change in dipole character of the molecule.

General assignments for stretching frequencies can be derived by the application of Hooke's law. In the application of the law, two atoms and their connecting bond are treated as two masses joined by a spring. Equation 1, derived from Hooke's law, states the relationship between frequency of oscillation, atomic masses, and the force constant of the bond.

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{f}{\frac{MxMy}{Mx + My}}\right)^{1/2} \qquad (1)$$

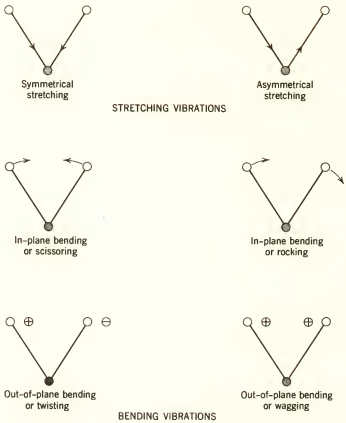


Fig. 1. Vibrational modes for AX_2 group. (⊕ and ⊖ represent relative movement at right angles to the surface of the page.)

where $\bar{\nu}$ = the vibrational frequency (cm^{-1})

c = velocity of light (cm/sec)

f = force constant of bond (dynes/cm)

Mx and My = mass of atom x and atom y, respectively (g).

The value of f is approximately 5×10^5 dynes per cm for single bonds and approximately two or three times this value for double bonds and triple bonds, respectively.

Application of the formula to C—H stretching, using 19.8×10^{-24} g and 1.64×10^{-24} g as mass values for C and H, respectively, places the frequency of the C—H bond vibration at 3040 cm^{-1} (3.30 μ). Actually, C—H stretching vibrations associated with methyl and methylene groups are observed in the general region between 2960–2850 cm^{-1} (3.38–3.51 μ). The calculation is not precise because effects arising from the environment of the C—H within a molecule have been ignored. When H is replaced by deuterium (C—D) the stretching vibrations occur at a lower frequency because of the effect of the heavier mass of D. The shift in absorption frequency following deuteration is often employed in the assignment of C—H stretching frequencies.

Similar calculations place the stretching frequencies of the following bonds in the general absorption regions indicated:

C—C, C—O, C—N	1300–800 cm^{-1} (7.7–12.5 μ)
C=C, C=O, C=N, N=O	1900–1500 cm^{-1} (5.3–6.7 μ)
C≡C, C≡N	2300–2000 cm^{-1} (4.4–5.0 μ)

To approximate the vibrational frequencies of bond stretching by Hooke's law, the relative contributions of bond strengths and atomic masses must be considered. For example, a superficial comparison of the C—H group with the F—H group, on the basis of atomic masses, might lead to the conclusion that the vibrational frequency of the F—H bond should occur at a lower frequency than that for the C—H bond. However, the increase in force constant from left to right across the first two rows of the periodic table has a greater effect than the mass increase. Thus, the F—H group absorbs at a higher frequency (4138 cm^{-1}, 2.42 μ) than the C—H group (2862 cm^{-1}, 3.49 μ).

Less energy is needed to produce bending than stretching vibrations of the same bond; bending vibrations are, therefore, found at lower frequencies. The broad ranges assigned to the principal stretching and bending frequencies are presented at the bottom of the group frequency chart (Figure 4).

The effects of hydrogen bonding on stretching and bending vibrations should be noted: Hydrogen bonding

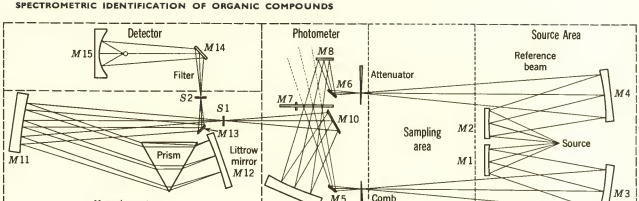


Fig. 2. Optical system of double-beam infrared spectrophotometer. (Courtesy of Perkin-Elmer Corporation, Norwalk, Conn.)

decreases stretching frequencies and increases bending frequencies.

INSTRUMENTATION

The modern double-beam infrared spectrophotometer consists of five principal sections: radiation source, sampling area, photometer, monochromator, and detector. A diagram of the optical system of a double-beam infrared spectrophotometer is shown in Figure 2.

Radiation Source

Infrared radiation is produced by electrically heating a source, usually a Nernst filament or a Globar to 1000–1800°C. The Nernst filament is fabricated from a binder and oxides of zirconium, thorium, and cerium. The Globar is a small rod of silicon carbide. The image of the source must be wider than the maximum width of the slits (vide infra). The maximum radiation energy from the Globar occurs in the 5500–5000 cm^{-1} (1.8–2.0 μ) region and drops off by a factor of about 600 as the 600 cm^{-1} (16.7 μ) region is approached. The Nernst filament furnishes maximum radiation energy at about 7100 cm^{-1} (1.4 μ) and drops by a factor of about 1000 as the lower frequency region is approached.

The radiation from the source is divided into two beams by mirrors *M*1 and *M*2. The two beams, reference beam and sample beam, are focused into the sample area by mirrors *M*3 and *M*4.

Sampling Area

Reference and sample beams enter the sampling area and pass through the reference cell and sampling cell, respectively. Opaque shutters, mounted on the source housing, permit blocking of either beam independently. The sampling area of a precision spectrophotometer accommodates a wide variety of sampling accessories varying from gas cells of 40 m effective path to microcells.

Photometer

The reference beam passes through the attenuator (vide infra) and is reflected by mirrors *M*6 and *M*8 to the rotating sector mirror *M*7, which alternately reflects the reference beam out of the optical system and transmits the beam to mirror *M*9. The reference beam is now an intermittent beam with a "frequency" of from 8 to 13 cycles per second depending on the particular instrument. This beam is focused by mirror *M*10 on the slit *S*1. The sample beam passes through the comb (vide infra) and is reflected by mirror *M*5 to the rotating sector mirror *M*7, which alternately transmits the beam out of the optical system and reflects it to mirror *M*9, thence to mirror *M*10 and slit *S*1.

At any given moment, the beam focused on slit *S*1 is either the reference beam, which was transmitted by the rotating sector mirror *M*7, or the sample beam, which was reflected by *M*7. In other words, the reference beam and the sample beam have been combined into a single beam of alternating segments; this establishes a switching frequency at the detector equal to the speed of rotation of *M*7.

When the beams are of equal intensity, the instrument is at an optical null. The comb in the sample beam permits balancing the beams. The recording pen is then at 100% transmittance when no sample is present.

The attenuator is driven in and out of the reference beam in response to the signal created at the detector (vide infra) by the sample beam. Thus, when the sample beam is absorbed by the sample, the attenuator is driven into the reference beam until its intensity matches that of the sample beam. It is the movement of the attenuator which is recorded by the recording pen.

Monochromator

The combined beam passes through the monochromator entrance slit *S*1 to the mirror *M*11, which reflects it through the prism to the Littrow mirror *M*12. At this point, the beam is dispersed by the prism over a range of frequencies (wavelengths). The dispersed beam is reflected back through the prism (to increase its dispersion) to mirror *M*11, thence to mirror *M*13, which focuses the beam on the exit slit *S*2. The width of the frequency range focused on the exit slit *S*2 is determined by the width of the entrance slit *S*1 and the dispersing power of the prism. The frequency range (that is, the region of the dispersed beam) focused on *S*2 at any one moment is determined by the angle of the Littrow mirror *M*12 at that moment. Thus, rotating *M*12 produces a scan of frequency ranges at the exit slit *S*2 and, consequently, at the detector.

Maximum resolution is obtained by using prism materials only in their range of greatest dispersing effectiveness. Each material has only a rather narrow effective range, and several materials should be used for greatest resolution over a spectral range. For example, calcium fluoride is most useful from 4200–1300 cm^{-1} (2.4–7.7 μ), whereas potassium or cesium bromide is most effective in the range 1100–385 cm^{-1} (9.1–26.0 μ). Sodium chloride prisms are widely accepted as a compromise material for the range 4000–650 cm^{-1} (2.5–15.4 μ), though they are somewhat deficient at the high frequency (short wavelength) end. The use of gratings instead of prisms is becoming more widespread.

The narrower the slit width, the greater is the resolution. Here again, some compromise is necessary because of the decreased energy output of the source at lower frequencies (longer wavelengths). On most instruments, the slit width is programmed to increase as the emitted source energy decreases, so that constant reference beam energy enters the monochromator.

Detector

After leaving the exit slit of the monochromator, the beam is reflected by a flat mirror *M*14 to an ellipsoidal mirror *M*15. The foci of the ellipsoidal mirror are the exit slit *S*2 and the detector.

The detector is a device which measures radiant energy by means of its heating effect. Two common types of detectors are the thermocouple and bolometer. In the thermocouple detector, the radiant energy heats one of two two-metal junctions and an emf is produced between the two junctions proportional to the degree of heating. The bolometer changes its resistance upon heating. It serves as one arm of a bridge so that a change in temperature will cause an unbalanced signal across the circuit. The unbalanced signal can be amplified and recorded or used to activate a servo mechanism to re-establish a balance.

Since the detector sees alternately the reference and the sample beam, at a switching frequency determined by the rotation of the sector mirror, any change in the intensity of the radiation due to absorption is detected as an off-null signal.

The amplified off-null signal of the detector is used to position the optical attenuator so that the radiation from the reference and sample beam are kept at equal intensity. The amount of attenuation required is a direct measure of the absorption by the sample. The movement of the attenuator is recorded by the recording chart pen.

SAMPLE HANDLING

Infrared spectra may be obtained on gases, liquids, or solids.

1. Gases and low-boiling liquids may be examined in a previously evacuated gas cell; these may be heated to extend the range of liquids which can be accommodated. Cells with effective pathlengths of several centimeters to 40 m are available.

2. Liquids may be examined neat or in solution. Neat liquids are examined between plates, with or without spacers (0.005–0.1 mm thick). Volatile liquids can be examined neat in sealed cells. The amount of material needed is between 1 mg and 10 mg.

Solutions are handled in cells from 0.1 mm to 1 mm in thickness. Concentrations are usually between 0.05 and 10%; the amount of solute required is in the range of 1 mg to 15 mg. A compensating cell of either fixed (matched with the sample cell) or variable thickness is placed in the reference beam. The spectrum thus obtained is that of the solute except in those regions in which the solvent absorbs strongly.

When only very small samples are available, ultramicro cavity cells are used in conjunction with a beam condenser. The smallest commercially available cell has a path length of approximately 0.05 mm and a capacity of approximately 0.5 microliters. A spectrum can thus be obtained on several micrograms of sample.

Solvents used must be dry and transparent in the frequency range of interest. Carbon tetrachloride, carbon disulfide, and chloroform are the three solvents most commonly used. Particular care should be exercised in selecting a solvent for compounds which are susceptible to hydrogen bonding effects. Carbon disulfide should not be used with primary or secondary amines. The transparent regions of selected solvents and mulling oils are presented in Figure 3.

3. Solids are examined as a mull, as a pressed disc, or as a deposited glassy film.

Mulls are prepared by grinding about 2 to 5 mg of the the solid with a drop of Nujol (a high-boiling petroleum

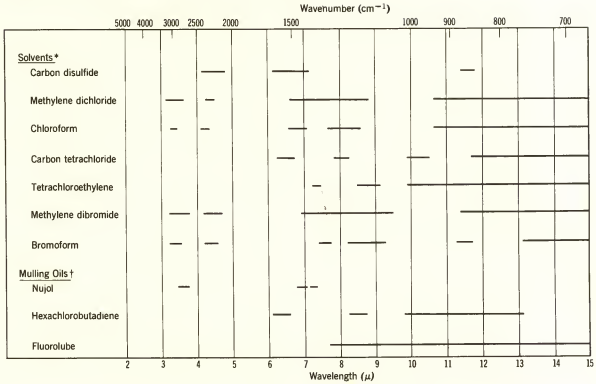


Fig. 3. Transparent regions of solvents and mulling oils. (*The open regions are those in which the solvent transmits more than 25% of the incident light at 1 mm thickness. † The open regions for mulling oils indicate transparency of thin films.

fraction), Fluorolube (a perfluorocarbon fraction), or hexachlorobutadiene with a mortar and pestle. The mull is examined as a thin film between salt plates. The transparent regions of these mulling oils are presented in Figure 3.

Pressed discs are made by pressing an intimate mixture (either ground, or mixed in a vibrator) of about 1 mg of the solid sample and approximately 100 mg of carefully dried potassium bromide. Pressing is usually carried out in a commercially available die under pressures of 20,000 to 50,000 lb per in.^{2}. It has recently been found that a mixture of about 1 mg of sample and 50 mg of potassium bromide can be placed in a hole punched out of an ordinary desk blotter and formed into a disc by pressing in a bench vise or a Carver press. Deposited films are only useful when the material can be deposited from solution, or cooled from a melt, as a glassy film.

In general, a dilute solution in a nonpolar solvent furnishes the best (that is, least distorted) spectrum. Nonpolar compounds give essentially the same spectra in the condensed phase (that is, neat liquid, a mull, a KBr disc, or a film) as they give in nonpolar solvents. Polar compounds, however, often show hydrogen bonding effects in the condensed phase. Unfortunately, polar compounds are frequently insoluble in nonpolar solvents, and the spectrum must be obtained either in a condensed phase, or in a polar solvent; the latter introduces the possibility of solute-solvent hydrogen bonding.

Reasonable care must be taken in handling salt cells and plates. Moisture-free samples should be used. Fingers should not come in contact with the optical surfaces. Care should be taken to prevent contamination with silicones which are hard to remove and have strong absorption patterns.

INTERPRETATION OF SPECTRA

Before an attempt is made to interpret a spectrum, three major requirements must be met: (1) The spectrum must be adequately resolved; (2) the spectrum should be that of a reasonably pure compound; and (3) the instrument should be calibrated so that the bands are observed at their proper frequencies or wavelengths. The latter can be assured by calibrating the instrument with a known sample such as a polystyrene film. The principal absorption frequencies for polystyrene have been rigorously established.

A precise treatment of the vibrations of a complex molecule is not feasible; thus, the infrared spectrum must be interpreted from empirical comparison of spectra, and extrapolations from studies of simpler molecules.

Many of the fundamental group frequencies vary over a rather wide range because of the complex vibrations occurring in a molecule. Certain of the frequencies, for

example those arising from the C—H and C=O stretching modes, remain within a fairly narrow region of the spectrum; shifts within this region can often serve to indicate some structural detail of the molecule. Any conclusions arrived at after examination of a particular band should be confirmed by examination of other portions of the spectrum. For example, the assignment of a C=O band to an aldehyde should be confirmed by observation of a band in the general region of 2750 cm^{-1} (3.63 μ) which results from a stretching vibration of the C—H bond of the aldehyde group. Similarly, the assignment of a carbonyl band to an ester should be confirmed by observation of a strong band in the 1310–1100 cm^{-1} (7.6–9.1 μ) region which arises from the C—O stretching of the ester group. Possible band shifts due to hydrogen bonding and interactions between solute and solvent must be kept in mind.

The two most important areas for a preliminary examination are in the regions above 1350 cm^{-1} (wavelengths below 7.40 μ) and in the 900–650 cm^{-1} (11.1–15.4 μ) region. The intervening bands are often complex, and are examined in the light of what is seen in the higher- and lower-energy regions of the spectrum.

Fortunately, a total interpretation of a spectrum is not needed for our purpose. Many questions arising in the interpretation of an infrared spectrum can be answered by data obtainable from the mass, ultraviolet, and NMR spectra.

CHARACTERISTIC GROUP FREQUENCIES OF ORGANIC MOLECULES

A table of characteristic group frequencies is presented as Figure 4. The ranges presented for group frequencies have been assigned following the examination of many compounds in which the groups occur. Although the ranges are quite well defined, the precise frequency or wavelength at which a specific group absorbs is dependent on its environment within the molecule and on its physical state.

This section of the chapter is concerned with a comprehensive look at these characteristic group frequencies and their relationship to molecular structure. No attempt has been made to present a detailed discussion of all of the available information concerning the group frequencies. This is available in the treatise of Jones and Sandorfy and that of Bellamy.

The coverage of compounds is limited to those containing C, H, O, N, S, and the halogens.

Normal Paraffins

The spectra of normal paraffins can be interpreted in terms of four types of bond vibrations, namely, the stretching and bending of C—H and C—C bonds. Detailed analysis of the spectra of the lower members of the alkane series has made possible detailed assignments of the spectral positions of specific vibrational modes. These vibration modes are common to most organic molecules. Although the positions of C—H stretching frequencies of methyl and methylene groups remain nearly constant in hydrocarbons, the attachment of $-CH_3$ or $-CH_2-$, to atoms other than carbon, may result in appreciable shifts of the C—H stretching and bending frequencies.

C—H *Stretching Vibrations*

Absorption, arising from C—H stretching in the alkanes, occurs in the general region around 3000–2840 cm^{-1} (3.3–3.5 μ). The positions of the C—H stretching vibrations are among the most stable in the spectrum.

METHYL GROUPS. An examination of a large number of saturated hydrocarbons containing methyl groups showed in all cases two distinct bands occurring at 2962 cm^{-1} (3.38 μ) and 2872 cm^{-1} (3.48 μ). The first of these results from a vibrational mode in which two C—H bonds of the methyl group are extending while the third one is contracting (asymmetric stretching). The second arises from symmetrical stretching in which all three of the C—H bonds expand and contract in phase. The presence of several methyl groups results in strong absorption at these positions. A methyl group directly attached to a benzene ring absorbs at 2924 cm^{-1} (3.42 μ).

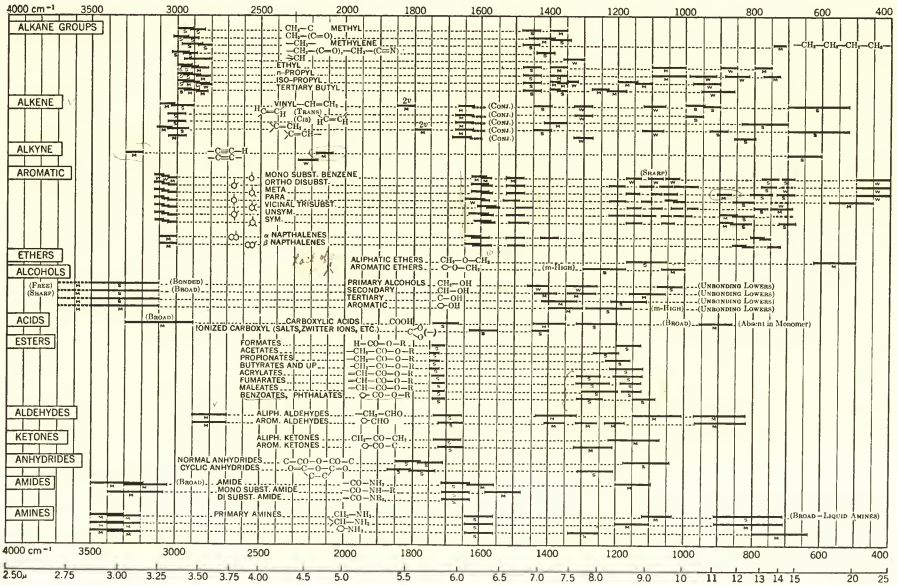
METHYLENE GROUPS. The methylene group produces an asymmetrical vibration at 2926 cm^{-1} (3.43 μ) and a symmetrical vibration at 2853 cm^{-1} (3.51 μ). The positions of these stretching bands do not vary more than ± 10 cm^{-1} in the aliphatic hydrocarbons and nonstrained cyclic hydrocarbons. Little variation from the assigned methylene position is observed for compounds such as diphenylmethane and benzyl alcohol. The frequency of methylene C—H stretching is increased when the methylene group is part of a strained ring system.

The presence of a double bond adjacent to a methyl or a methylene produces some splitting of the lower frequency band to give a double band whose mean frequency remains nearly the same as the nonsplit band.

C—H *Bending Vibrations*

METHYL GROUPS. Two bending vibrations of the methyl group can occur. One of these is a symmetrical vibration near 1375 cm^{-1} (7.28 μ). The other, the asymmetrical vibration, occurs near 1450 cm^{-1} (6.90 μ).

The asymmetrical vibration at 1450 cm^{-1} (6.90 μ) may overlap with the scissoring vibration of the methylene group (vide infra). The two vibrations are generally


4000 cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
ALKANE GROUPS
METHYL
METHYLENE
ETHYL
n-PROPYL
ISO-PROPYL
TERTIARY BUTYL
ALKENE
VINYL
(TRANS)
(CIS)
(CONJ.)
ALKYNE
AROMATIC
MONO SUBST. BENZENE
ORTHO DISUBST.
META
PARA
VICINAL TRISUBST.
UNSYM.
SYM.
α NAPTHALENES
β NAPTHALENES
(SHARP)
ETHERS
ALIPHATIC ETHERS
AROMATIC ETHERS
(m-HIGH)
ALCOHOLS
(FREE)
(SHARP)
(BONDED)
(BROAD)
PRIMARY ALCOHOLS
SECONDARY
TERTIARY
AROMATIC
(UNBONDING LOWERS)
(m-HIGH)
ACIDS
CARBOXYLIC ACIDS
(BROAD)
(ABSENT IN MONOMER)
IONIZED CARBOXYL (SALTS, ZWITTER IONS, ETC.)
ESTERS
FORMATES
ACETATES
PROPIONATES
BUTYRATES AND UP
ACRYLATES
FUMARATES
MALEATES
BENZOATES, PHTHALATES
ALDEHYDES
ALIPH. ALDEHYDES
AROM. ALDEHYDES
KETONES
ALIPH. KETONES
AROM. KETONES
ANHYDRIDES
NORMAL ANHYDRIDES
CYCLIC ANHYDRIDES
AMIDES
AMIDE
MONO SUBST. AMIDE
DI SUBST. AMIDE
AMINES
PRIMARY AMINES
(BROAD – LIQUID AMINES)
4000 cm⁻¹
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
2.50μ
2.75
3.00
3.25
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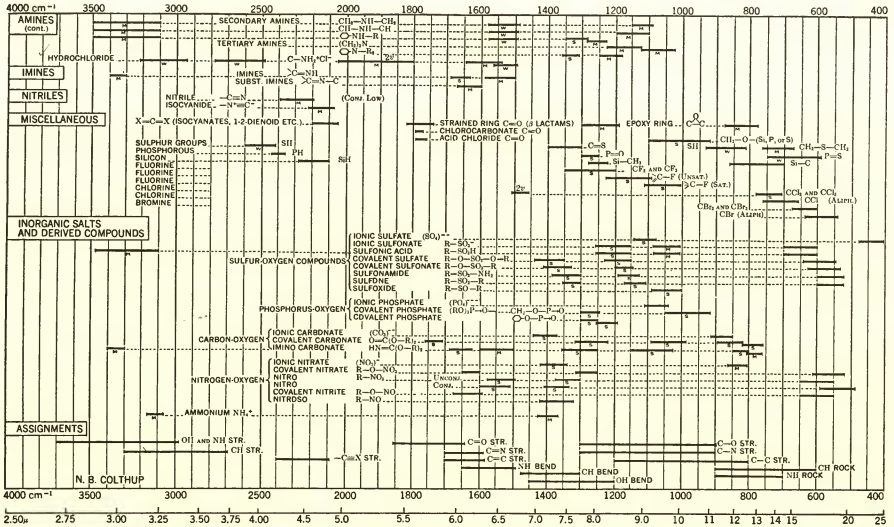


Fig. 4. Characteristic infrared group frequencies. (Courtesy of N. B. Colthup, Stamford Research Laboratories, American Cyanamid Company, and the editor of the *Journal of the Optical Society*.) Overtone bands are marked 2*p*.

discernible in the spectra of low molecular weight hydrocarbons and in compounds such as diethyl ketone in which the methylene scissoring band has been shifted to a longer wavelength due to its proximity with the carbonyl group.

The absorption band near 1375 cm^{-1} (7.28 μ), arising from the symmetrical bending of the C—H bonds, is very stable in position when the methyl group is attached to another carbon atom. The intensity of this band is greater for each methyl group in the compound than that for the asymmetrical methyl vibration or the methylene scissoring vibration.

METHYLENE GROUPS. The bending vibrations of the C—H bonds in the methylene group have already been shown schematically in Figure 1. The four bending vibrations are referred to as scissoring, rocking, wagging, and twisting.

The scissoring vibration band occurs at a very constant position near 1465 cm^{-1} (6.83 μ). The conflict between this band and that arising from the asymmetrical methyl bending has already been pointed out.

The band resulting from the methylene rocking vibration appears in the general region of 720 cm^{-1} (13.9 μ). In the lower members of the *n*-paraffin series the band may appear at somewhat higher frequencies (shorter wavelengths), but for compounds C_7 and above, the value is constant at 720 cm^{-1} (13.9 μ). This band is observed in the spectra of all compounds which contain a methylene chain of four or more carbon atoms.

Absorption of hydrocarbons due to methylene twisting and wagging vibrations are observed in the 1350–1150 cm^{-1} (7.4–8.7 μ) region. These bands are appreciably weaker than those resulting from methylene rocking or scissoring.

C—C *Stretching Vibrations*

The bands assigned to C—C stretching vibrations in the broad region of 1200–800 cm^{-1} (8.3–12.5 μ) are very weak and are generally of little value for identification.

C—C *Bending Vibrations*

The C—C bending vibrations of hydrocarbons occur at very low frequencies (below 500 cm^{-1}, above 20 μ).

Branched Chain Hydrocarbons

In general, the changes brought about in the spectrum of a hydrocarbon by branching result from changes in skeletal stretching vibrations and methyl and methylene bending vibrations; these occur below 1500 cm^{-1} (above 6.7 μ). The significance of these changes is best assessed by comparison with spectra of known structures.

C—H *Stretching Vibrations*

TERTIARY C—H GROUPS. Absorption resulting from this vibrational mode is very weak. An assignment has been made at 2890 cm^{-1} (3.46 μ).

C—H *Bending Vibrations*

GEMINAL DIMETHYL GROUPS. Configurations in which two methyl groups are attached to the same carbon atom exhibit distinct spectra in the C—H bending region. The isopropyl group shows a strong doublet, with peaks of almost equal intensity, at 1385–1380 cm^{-1} (7.22–7.25 μ) and 1370–1365 cm^{-1} (7.30–7.33 μ). The tertiary butyl group gives rise to two C—H bending bands at 1395–1385 cm^{-1} (7.17–7.22 μ) and 1365 cm^{-1} (7.33 μ).

The isopropyl group also gives rise to a moderately strong band in the 1175–1165 cm^{-1} (8.51–8.58 μ) region and a weak band in the 840–790 cm^{-1} (11.90–12.66 μ) region.

When the gem-dimethyl group occurs at an internal position in a hydrocarbon chain, two bands are observed at 1385–1375 cm^{-1} (7.22–7.28 μ) and 1372–1362 cm^{-1} (7.29–7.35 μ).

Cycloparaffins

C—H *Stretching Vibrations*

The methylene stretching vibrations, as observed in aliphatic compounds, remain much the same for cyclic polymethylene structures provided the ring is unstrained. Strain increases the C—H stretching frequency. Bromocyclopropane shows bands at 3077 and 2985 cm^{-1} (3.25 and 3.35 μ).

C—H *Bending Vibrations*

Cyclization decreases the frequency of the methylene scissoring vibration: 1468 cm^{-1} (6.82 μ) for *n*-hexane and 1452 cm^{-1} (6.90 μ) for cyclohexane.

Olefinic Hydrocarbons

C=C *Stretching Vibrations*

LINEAR OLEFINS. The C=C band of nonconjugated olefins is usually found at 1660–1640 cm^{-1} (6.0–6.1 μ) and is weak; it is very weak or absent in such symmetrical molecules as tetrachloroethylene, which can be used as a solvent. *Cis* olefins absorb more strongly than *trans*

olefins; terminal double bonds absorb more strongly than internal double bonds.

CYCLOOLEFINS. The C=C stretching frequency of cycloolefins is in the same general range as that for acyclic olefins. The effect of strain in the ring is evidenced by a reduction in the frequency of absorption as the ring becomes smaller. Cyclohexene shows a C=C absorption at 1646 cm^{-1} (6.08 μ), whereas cyclobutene absorbs at 1566 cm^{-1} (6.39 μ). The weak absorption band resulting from C=C is often obscured by the C=O stretching band in compounds containing C=O which is not conjugated with the olefinic double bond.

CONJUGATED SYSTEMS. Conjugated dienes, without a center of symmetry, show two absorption bands; one near 1600 cm^{-1} (6.25 μ), the other near 1650 cm^{-1} (6.06 μ). The latter band is the more intense.

The band near 1600 cm^{-1} (6.25 μ) distinguishes the conjugated system from the single olefinic bond which absorbs weakly in the 1660–1640 cm^{-1} (6.0–6.1 μ) region.

Conjugation of the olefinic double bond, with an aromatic ring, results in enhanced olefinic absorption near 1625 cm^{-1} (6.15 μ). In the conjugated system an aromatic C=C stretching absorption band occurs near 1590 cm^{-1} (6.28 μ).

OLEFINS CONTAINING FUNCTIONAL GROUPS. The substitution of the ethylenic hydrogen atoms by chlorine, bromine, iodine or other electronegative groups generally lowers the frequency of the C=C stretching. Fluorine has an opposite effect and the C=C stretching frequency for $CCl_2{=}CF_2$ and for $CH_2{=}CF_2$ occurs near 1730 cm^{-1} (5.78 μ).

Olefinic C—H *Stretching Vibrations*

In general, any C—H stretching bands below 3000 cm^{-1} (above 3.33 μ) can be attributed to alkyl groups, whereas those above 3000 cm^{-1} (below 3.33 μ) result from aromatic or olefinic C—H stretching. Exceptions to be noted, however, are the C—H stretching in small rings such as cyclopropane and C—H stretching in halogenated alkyl groups. The frequency of the olefinic C—H stretching band is influenced by substitution on the C=C; for example, when the double bond is singly substituted on both carbon atoms ($R_1HC{=}CHR_2$) the absorption band occurs at 3030–3010 cm^{-1} (3.30–3.32 μ). The C—H stretching of the vinyl group is most easily distinguished because of its intensity and occurrence between 3075–3090 cm^{-1} (3.25–3.24 μ). When the C=C is triply substituted, the remaining C—H vibration is usually too weak to be observed.

Olefinic C—H *Bending Vibrations*

Olefinic C—H bonds can undergo bending either in the same plane as the C=C bond, or perpendicular to it. The bending vibrations can either be in-phase or out-of-phase with respect to one another. The most characteristic vibrational mode of olefins is the out-of-plane, in-phase vibration between 1000–800 cm^{-1} (10.0–12.5 μ).

The in-plane C—H bending vibration, for *trans* disubstituted ethylenes, produces a strong band in the 1310–1290 cm^{-1} (7.64–7.75 μ) region. *cis*-Disubstituted ethylenes frequently absorb near 1405 cm^{-1} (7.12 μ). Two C—H in-plane bending bands are observed in the spectra of monosubstituted ethylenes (vinyl). The low frequency (long wavelength) band, 1300–1290 cm^{-1} (7.70–7.75 μ), is attributed to the —CH=C— structure, whereas the high frequency (short wavelength) band, 1420–1410 cm^{-1} (7.04–7.10 μ), is attributed to the $-C{=}CH_2$ structure.

The out-of-plane bending vibrations for olefinic C—H groups are observed at wavelengths greater than 10 μ. The positions and intensities of absorption for *cis*, *trans*, and vinyl structures can be summarized as follows.

trans (—CH=CH—)
970–960 cm^{-1} (10.3–10.42 μ) (*s*)

cis (—CH=CH—)
Near 690 cm^{-1} (14.50 μ)
(variable in position and intensity)

Vinyl (—CH=CH_2)
995–985 cm^{-1} (10.05–10.15 μ) (*s*)
915–905 cm^{-1} (10.92–11.05 μ) (*s*)

2,2-Disubstituted ($\rangle C{=}CH_2$)
855–885 cm^{-1} (11.17–11.3 μ) (*s*)

(*s*) Strong.

The out-of-plane C—H bending frequency of *cis* disubstituted ethylenes is more affected by changes in the surrounding structure than the absorption frequency of the *trans* isomer. The substitution of chlorine, methyl or an oxygenated group in the α-position of the *cis* isomer results in a shift of absorption to a higher frequency (shorter wavelength).

Acetylenic Hydrocarbons

The two stretching vibrations in acetylenic molecules involve the C≡C stretching and the ≡C—H stretching.

C≡C *Stretching Vibrations*

The C≡C stretching band is weak. Because of the symmetry of the molecules, this band does not appear for acetylene and symmetrically disubstituted acetylenes. The terminal group C≡C produces a stronger band than do internal C≡C groups. The weak C≡C stretching vibration occurs at 2140–2100 cm^{-1} (4.67–4.76 μ) for monosubstituted acetylenes and at 2260–2190 cm^{-1} (4.43–4.57 μ) for 1,2-disubstituted acetylenes.

C—H *Stretching Vibrations*

Two strong characteristic bands are observed in infrared spectra of monosubstituted acetylenes. One occurs at 3305–3270 cm^{-1} (3.03–3.06 μ) and arises from the C—H stretching vibration. The other occurs between 600–650 cm^{-1} (16.7–15.4 μ) and results from C—H bending vibrations. The latter is not observed in spectra which terminate at 650 cm^{-1} (15.4 μ).

The N—H stretching band may occur in the same region as the acetylenic C—H stretching band, but the N—H stretching bands are usually broader than those arising from C—H stretching.

Mononuclear Aromatic Hydrocarbons

The most prominent bands in the spectra of aromatic compounds occur in the low frequency region of 900–650 cm^{-1} (11.1–15.4 μ). These strong absorption bands result from the out-of-plane bending of the ring C—H bonds. Stretching vibrations resulting from the C to C bonds in the ring fall in the region of 1610–1480 cm^{-1} (6.21–6.76 μ). A characteristic absorption band occurs between 3100–3300 cm^{-1} (3.23–3.33 μ) in the high frequency (short wavelength) end of the spectrum resulting from ring C—H stretching. Weaker combination and overtone bands in the 2000–1650 cm^{-1} (5.00–6.06 μ) are highly characteristic of the substitution pattern but can only be observed in concentrated solutions using thick samples. They are also masked by C=C and C=O stretching vibration bands.

Out-of-Plane Bending Vibrations

The positions of out-of plane deformation or bending vibrations are largely dependent upon the position of substitution rather than the nature of the substituent. Consequently, the location of the bands between 900–650 cm^{-1} (11.1–15.4μ) is often used to determine the positions of substitution, and because of the high intensities of the bands, they have been treated quantitatively to obtain the relative concentrations of ortho- , meta- , and para-substituted isomers in mixtures.

The assignments made for the various substituted benzenes are summarized in Table I. These are reliable for alkyl substituents but should be used with caution with polar substituents.

Aromatic C—H *Stretching Vibrations*

The aromatic C—H stretching vibration occurs in the region between 3100–3000 cm^{-1} (3.23–3.33 μ), the same area in which the C—H stretching of olefins is observed.

Aromatic C=C *Stretching Vibrations*

Skeletal vibrations of aromatic rings result in absorption in the region of 1610–1480 cm^{-1} (6.21–6.76 μ). In the spectra of substituted benzenes, bands are commonly observed in the 1610–1590 cm^{-1} (6.21–6.29 μ) region and in the 1500–1480 cm^{-1} (6.67–6.76 μ) region. Benzene derivatives containing complex substitution may absorb at other frequencies within this general region.

Table I* C—H *Out-of-Plane Bending and Benzene Ring Substitution*

SUBSTITUTION POSITION	BAND POSITIONS (cm^{-1}, μ)	BAND STRENGTH
Benzene	670 (14.9)	*s*
Monosubstitution	770–730 (12.99–13.70)	*s*
	710–690 (14.08–14.49)	*s*
1,2 disubstitution	770–735 (12.99–13.61)	*s*
1,3 disubstitution	900–860 (11.11–11.63)	*m*
	810–750 (12.35–13.33)	*s*
	725–680 (13.74–14.71)	*m*
1,4 and 1,2,3,4 substitution	860–800 (11.63–12.50)	*s*
1,2,3 trisubstitution	800–770 (12.50–12.99)	*s*
	720–685 (13.89–14.60)	*m*
1,2,4 trisubstitution	860–800 (11.63–12.50)	*s*
	900–860 (11.11–11.63)	*m*
1,3,5 trisubstitution	900–860 (11.11–11.63)	*m*
	865–810 (11.56–12.35)	*s*
	730–675 (13.70–14.81)	*s*
1,2,3,5–1,2,4,5 and 1,2,3,4,5 substitution	900–860 (11.11–11.63)	*m*

* Reprinted by permission from A. D. Cross, *Introduction to Practical Infra-red Spectroscopy*, Butterworths Scientific Publications, London, 1960.

Polynuclear Aromatic Compounds

Polynuclear aromatic compounds, like the mononuclear aromatics, show characteristic absorption in three regions of the spectrum.

The aromatic C—H stretching and skeletal vibrations result in absorption in the same regions as observed for the mononuclear aromatics.

The most characteristic absorption of polynuclear aromatics is in the 900–650 cm^{-1} (11.1–15.4 μ) region. The numerous intense bands in this region are characteristic of polynuclear structures and offer the best information for identification of specific ring systems. For identification purposes, the spectrum of an unknown compound should be compared with the spectra of known compounds.

Alcohols and Phenols

The most conspicuous bands observed in the spectra of alcohols and phenols result from O—H stretching vibrations. C—O stretching bands and O—H bending vibration bands are also observed.

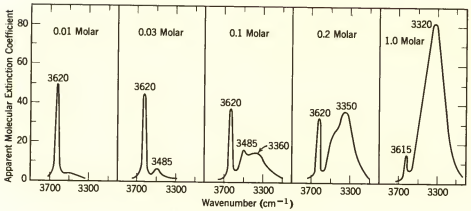


Fig. 5. Infrared spectrum of the O—H stretching region of cyclohexanol in carbon tetrachloride. (Reproduced by permission from R. N. Jones, and C. Sandorfy, "The Application of Infrared and Raman Spectrometry to Elucidation of Molecular Structure" Chapter IV, Vol. IX, in A. Weissberger, *Technique of Organic Chemistry*, Interscience, New York, 1956, p. 418.)

O—H *Stretching Vibrations*

The unbonded or free hydroxyl group absorbs strongly in the range of 3700–3500 cm^{-1} (2.72–2.86 μ). These bands are only observed in the vapor phase or in high dilution in nonpolar solvents. The position of the free O—H band is not very sensitive to changes in molecular structure.

Intermolecular bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies (3360–3350 cm^{-1}, 2.90–2.99 μ) at the expense of the free hydroxyl band. This effect is illustrated in Figure 5 in which the absorption in the O—H stretching region is shown for five different concentrations of cyclohexanol in carbon tetrachloride solution.

In the case of di- and polyhydric alcohols, association may take place intramolecularly as well as intermolecularly resulting in a somewhat more complex spectrum in which the intramolecular bonding is unaffected by dilution in a nonpolar solvent. Chelation results in a broad band between 3200 and 2500 cm^{-1} (3.13 and 4.00 μ).

C—O *Stretching and* O—H *Bending*

Most alcohols and phenols exhibit two absorption bands in the 1420–1000 cm^{-1} (7.05–10.00 μ) region. These bands are sensitive to hydrogen bonding, that is, move to lower frequencies (longer wavelengths) upon dilution. The band in the region of 1420–1340 cm^{-1} (7.05–7.47 μ) likely results from O—H bending. The bands in the 1230–1000 cm^{-1} (8.13–10.00 μ) regions are attributed to —C—OH stretching. The lower frequency band, which is usually more intense, has been assigned quite narrow frequency ranges for primary, secondary, and tertiary alcohols and phenols. The following assignments have been made for alcohols and phenols observed as liquids.

Straight-chain primary alcohols	1075–1010 cm^{-1} (9.30–9.90 μ)
Secondary alcohols	1120–1105 cm^{-1} (8.93–9.05 μ)
Tertiary alcohols	1170–1100 cm^{-1} (8.55–9.09 μ)
Phenols	1230–1140 cm^{-1} (8.13–8.77 μ)

The position of C—OH stretching absorption is influenced by the nature of the structure in the vicinity of the hydroxyl group. Chain-branching at the α-carbon atom reduces the frequency of absorption by 10–15 cm^{-1}. α,β-Unsaturation lowers the frequency. α,β-Unsaturated secondary alcohols absorb in the general region of 1074–1012 cm^{-1} (9.31–9.88 μ).

The spectra of alcohols, determined in the liquid state, show broad absorption bands in the 750–650 cm^{-1} (13.35–15.40 μ) region as a result of out-of-plane bending of the bonded OH group.

Ethers and Peroxides

The characteristic response of ethers in the infrared is associated with the stretching vibrations of the C—O—C system. Since the vibrational characteristics of this system would not be expected to differ greatly from the C—C—C system, it is not surprising to find the response to C—O—C stretching in the same general region. However, since vibrations involving oxygen atoms result in greater dipole moment changes than those involving saturated carbon atoms, more intense infrared bands are observed for ethers.

The asymmetrical C—O—C stretching vibration gives a strong band between 1250–1060 cm^{-1} (8.00–9.43 μ). In the aliphatic ethers, the band occurs in the 1150–1060 cm^{-1} (8.70–9.43 μ) region, usually close to 1100

cm^{-1} (9.10 μ). Diisopropyl ether shows a triplet structure in the 1170–1100 cm^{-1} (8.55–9.09 μ) region attributed to branching on the α-carbons. Aryl, aralkyl, or vinyl ethers absorb in the 1270–1230 cm^{-1} (7.87–8.13 μ) region. Carboxylic esters and lactones also absorb strongly in the same regions.

Aliphatic peroxides absorb in the general region of 890–830 cm^{-1} (11.24–12.50 μ). Acyl and aroyl peroxides have two characteristic frequencies arising from the carbonyl groups in the region of 1820–1755 cm^{-1} (5.50–5.70 μ).

Ketones

Ketones, aldehydes, carboxylic acids, carboxylic esters, lactones, acid halides, and anhydrides (also amides and lactams, which are discussed under nitrogen compounds) show a strong C=O stretching absorption band in the region of 1870–1540 cm^{-1} (5.35–6.50 μ). Its relatively constant position, its high intensity, and its relative freedom from interference make it one of the easiest bands to recognize in infrared spectra.

Within its given range, the position of the C=O stretching band is determined by the following factors: (1) the physical state; (2) electrical and mass effects of neighboring substituents; (3) conjugation; (4) ring strain; and (5) hydrogen bonding (intermolecular and intramolecular). Consideration of these factors leads to a considerable amount of information about the environments of the C=O group.

C=O *Stretching Vibrations*

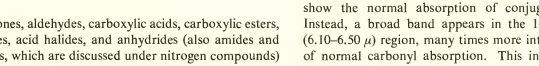
The C=O stretching vibration of aliphatic ketones and six-membered or larger cyclic ketones in nonpolar solvents lies between 1725 and 1705 cm^{-1} (5.80–5.87 μ). In the liquid state, (neat), the absorption is shifted to 1747–1714 cm^{-1} (5.73–5.83 μ). In general, absorption in the solid state is shifted to somewhat lower frequencies (longer wavelengths) by crystal lattice forces.

Substitution of a halogen atom directly on the C=O group has a pronounced effect on the position of the absorption band. Acid chlorides, for example, absorb at 1815–1785 cm^{-1} (5.51–5.60 μ). A chlorine in the α-position shifts the absorption of a normal ketone about 20 cm^{-1} to higher frequency (0.07 μ to shorter wavelength). α-Fluorinated ketones have been reported to absorb at frequencies as high as 1770 cm^{-1} (5.65 μ).

Conjugation of the C=O with an ethylenic group decreases the vibrational frequency to 1685–1666 cm^{-1} (5.93–6.00 μ). Additional conjugation may cause a slight further reduction in frequency. The frequency of the C=C bond involved in the conjugation is also lowered. Conjugation of the C=O with a benzene ring decreases the vibrational frequency to 1700–1680 cm^{-1} (5.88–5.95 μ); ring substituents show some effect on the C=O absorption. Conjugated C=O groups, that is, α-diketones, show only a single band with very slight, if any, increase in frequency over that of a monoketone. Presumably, α-diketones are in the *trans* configuration, and the symmetrical vibration is forbidden.

Ring strain in a ring containing a C=O group results in an increase in the C=O stretching frequency. Thus, cyclobutanone absorbs near 1775 cm^{-1} (5.64 μ) and cyclopentanones from 1750–1740 cm^{-1} (5.72–5.75 μ), compared to cyclohexanones at 1725–1705 cm^{-1} (5.80–5.87 μ).

1,3-Diketones, which exist in the monoenol form, do not show the normal absorption of conjugated ketones. Instead, a broad band appears in the 1640–1540 cm^{-1} (6.10–6.50 μ) region, many times more intense than that of normal carbonyl absorption. This intense and displaced absorption probably results from intramolecular hydrogen bonding, the double bond character of the carbonyl being reduced by resonance:



The enol O—H stretching absorption is seen as a broad band at 2700–2500 cm^{-1} (3.71–4.00 μ).

Methylene and Methyl Bending in Ketones

In aliphatic hydrocarbons, the methylene scissoring vibration occurs at 1465 cm^{-1} (6.83 μ). When a methylene group is α to the C=O group, the C—H absorption band falls into the 1435–1405 cm^{-1} (6.97–7.12 μ) region. Ketones containing an α-methyl group show a displacement of the symmetrical C—H methyl bending frequency [1380–1370 cm^{-1} (7.25–7.31 μ) in hydrocarbons] to 1360–1355 cm^{-1} (7.35–7.38 μ).

Aldehydes

C=O *Stretching Vibrations*

Aliphatic aldehydes have a C=O absorption at 1740–1720 cm^{-1} (5.75–5.82 μ). This absorption is subject to much the same influences as were noted for ketones.

Unsaturation in the α,β-position brings about a reduction of the C=O stretching frequency to 1705–1685 cm^{-1} (5.87–5.94 μ). Additional conjugation results in only a slight further lowering of the frequency. The carbonyl absorption range for aryl aldehydes falls between 1715–1695 cm^{-1} (5.83–5.90 μ), and is affected by ring substituents. α-Dialdehydes show only a single peak with little or no shift. Glyoxal, for example, absorbs at about the same frequency as formaldehyde.

C—H *Stretching Vibrations*

The C—H stretching vibration in aldehydes

$$\left(\begin{array}{c} \text{O} \\ \| \\ \text{in the C—H group} \end{array}\right)$$

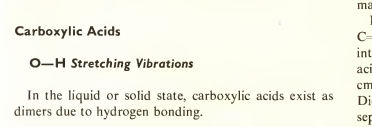
results in a characteristic absorption at 2880–2650 cm^{-1} (3.47–3.77 μ).

The appearance of a band near 2720 cm^{-1} (3.68 μ), accompanied by a carbonyl absorption band, is good evidence for the presence of an aldehyde group.

Carboxylic Acids

O—H *Stretching Vibrations*

In the liquid or solid state, carboxylic acids exist as dimers due to hydrogen bonding.



The exceptional strength of the hydrogen bonding is explained on the basis of a large contribution of an ionic resonance structure. As a result of this strong bonding, a free O—H stretching vibration is observed for carboxylic acids only in very dilute solution in nonpolar solvents, or in the vapor phase. In both cases, a mixture of monomer and dimer is observed.

Carboxylic acids display very broad, bonded O—H stretching absorption in the region of 3300–2500 cm^{-1} (3.03–4.00 μ). This band, in the region 2700–2500 cm^{-1} (3.71–4.00 μ), often consists of a continuous series of small bands.

Since few other compounds absorb in the 2700–2500 cm^{-1} (3.71–4.00 μ) region, this region is valuable for the identification of carboxylic acids. Conclusions resulting from the examination of the 2700–2500 cm^{-1} (3.71–4.00 μ) region should be tempered by an examination of other portions of the spectrum, particularly the carbonyl region. Other structures containing strong hydrogen bonding such as enolic β-diketones, will also absorb strongly in the 2700–2500 cm^{-1} (3.71–4.00 μ) region, but the C=O stretching vibration is shifted to frequencies lower than those observed for carboxylic acids.

C=O *Stretching Vibrations*

The C=O group in saturated aliphatic acids absorbs between 1725–1700 cm^{-1} (5.80–5.88 μ) when examined as a solid, a liquid, or in concentrated solution; this is the C=O stretching vibration frequency for the dimer. Replacement of α-hydrogens with a halogen or other electronegative group shifts the C=O absorption to a higher frequency (shorter wavelength). The C=O absorption for α-chloropropionic acid, for example, occurs at 1730 cm^{-1} (5.78 μ).

In general, α,β-unsaturated and aryl-conjugated acids absorb at 1700–1680 cm^{-1} (5.88–5.95 μ). Extension of the conjugation beyond the α,β-position results in very little additional shifting of the C=O absorption. Substitution in the aryl portion of aryl carboxylic acids affects the position of the observed C=O frequency in the same manner observed for aldehydes.

Internal hydrogen bonding reduces the frequency of C=O stretching absorption to a greater extent than does intermolecular hydrogen bonding. For example, fumaric acid absorbs at 1680 cm^{-1} (5.95 μ), maleic acid at 1705 cm^{-1} (5.87 μ), and salicylic acid at 1655 cm^{-1} (6.04 μ). Dicarboxylic acids, in which the carboxyl groups are separated by three or more carbon atoms, show normal carboxyl absorption. Malonic acid shows two C=O absorptions, at 1740 cm^{-1} (5.75 μ) and at 1710 cm^{-1} (5.85 μ).

The spectra of acids with halogens in the α-position, determined in the liquid state or in solution, show dual carbonyl bands due to rotational isomerism. The higher frequency (shorter wavelength) band corresponds to the more polar structure in which the halogen is in close proximity with the carbonyl group.

The C=O absorption bands of carboxylic acids are generally more intense than those of ketones.

C—O *Stretching and* O—H *Bending Vibrations*

Two bands, arising from C—O stretching or O—H bending, appear in the spectra of carboxylic acids near 1440–1395 cm^{-1} (6.95–7.17 μ) and 1320–1210 cm^{-1} (7.58–8.28 μ). The band near 1400 cm^{-1} (7.14 μ) is generally weak and may not be observed. The band near 1250 cm^{-1} (8.00 μ) is strong, and usually appears as a doublet in the spectra of long-chain fatty acids.

Carboxylate Ion Stretching Vibrations

The carboxylate ion gives rise to two bands: an asymmetrical stretching band at 1610–1550 cm^{-1} (6.22–6.45 μ), and a symmetrical stretching band at 1400–1300 cm^{-1} (7.15–7.70 μ). The former band is generally stronger and more characteristic.

Esters and Lactones

Esters and lactones have two characteristic absorption bands: C=O stretching and C—O stretching. The

intense C=O stretching vibration occurs at higher frequencies (shorter wavelengths) than that of normal ketones. Overlapping occurs between esters in which the C=O frequency is lowered and ketones in which the normal ketone vibration is raised. A distinguishing feature of esters and lactones, however, is the strong C—O stretching band which occurs in the region where relatively weak bands would arise from C—C stretching in the ketones. There is overlapping in the C=O frequency of esters or lactones and acids, but the O—H vibration and the possibility of salt formation distinguish the acids.

The frequency of the ester C=O responds to environmental changes in the vicinity of the carbonyl group in much the same manner as ketones.

C=O *Stretching Vibrations*

The C=O absorption band of saturated aliphatic esters (except formates) is at 1740 cm^{-1} (5.75 μ). The C=O absorption bands of formates, α,β-unsaturated, and aryl esters are in the region of 1730–1715 cm^{-1} (5.78–5.83 μ). Further conjugation has little or no additional effect.

In the case of vinyl esters, the $-C(=O)-O-C=C-$ structure results in a marked raising of the carbonyl frequency; for example, vinyl acetate has a carbonyl band absorption at 1776 cm^{-1} (5.63 μ). Phenyl acetate absorbs at 1770 cm^{-1} (5.65 μ).

α-Halogen substitution results in a rise in the C=O vibrational frequency. Ethyl trichloroacetate absorbs at 1770 cm^{-1} (5.65 μ). The results of fluorine substitution are still more marked.

In α-diesters and α-keto esters, as in α-diketones, there appears to be little interaction between the two carbonyl groups so that normal absorption occurs in the region of 1755–1740 cm^{-1} (5.70–5.75 μ). In the case of β-keto esters, however, where enolization can occur, an additional band is observed at 1650 cm^{-1} (6.07 μ), which results from bonding between the C=O and the enolic hydroxyl group.

Little or no interaction takes place between the C=O groups of γ- or δ-diesters, or γ- or δ-keto esters. Diethylsuccinate, for example, absorbs at 1730 cm^{-1} (5.78 μ).

The carbonyl absorption of δ-lactones (six-membered ring) occurs in the same region as observed for conventional esters. Such lactones, however, will exhibit a reduction in the carbonyl frequency (increase in wavelength) when the ring possesses unsaturation or α-substitution.

Saturated γ-lactones (five-membered ring) absorb at shorter wavelengths than open-chain esters. γ-Valerolactone, for example, shows carbonyl absorption at 1770 cm^{-1} (5.65 μ). α,β-Unsaturated γ-lactones show a lowering of the C=O absorption frequency of about 20 cm^{-1} (to 1750 cm^{-1}, 5.71 μ) in comparison to the saturated γ-lactone.

C—O *Stretching Vibrations*

The C—O stretching mode of esters, ethers, acids, and alcohols gives rise to bands in the 1300–1100 cm^{-1} (7.70–9.10 μ) region. Despite the fact that these bands have considerable intensity, they are sometimes difficult to recognize because of other bands occurring in the region. They are much less stable in position than are the carbonyl bands. In the case of esters, however, the frequency of this band is important, since its position appears to be stabilized by the C=O group. The following assignments have been made for the C—O stretching vibrations for several esters.

Formates	Near 1190 cm^{-1} (8.41 μ)
Acetates	Near 1245 cm^{-1} (8.03 μ)
Propionates	Near 1190 cm^{-1} (8.41 μ)
n-Butyrates	Near 1190 cm^{-1} (8.41 μ)
iso-Butyrates	Near 1200 cm^{-1} (8.33 μ)
iso-Valerates	Near 1195 cm^{-1} (8.37 μ)

The methyl esters of long-chain fatty acids present a three-band pattern with bands near 1250 cm^{-1} (8.00 μ), 1205 cm^{-1} (8.30 μ), and 1175 cm^{-1} (8.50 μ). The band at 1175 cm^{-1} (8.50 μ) is the strongest.

Esters of α,β-unsaturated acids and esters of aromatic acids show two strong absorption bands, one in the region of 1310–1250 cm^{-1} (7.63–8.00 μ) and one in the region of 1200–1100 cm^{-1} (8.33–9.09 μ). Absorption, due to C—O stretching in lactones, is observed in the 1250–1370 cm^{-1} (8.00–9.00 μ) region.

Acid Halides and Anhydrides

C=O *Stretching Vibrations*

Both the acid halides and anhydrides show strong absorption in the C=O region. The unconjugated acid halides absorb between 1815–1785 cm^{-1} (5.51–5.60 μ); the conjugated acid halides absorb in a slightly lower frequency range of 1800–1770 cm^{-1} (5.56–5.65 μ).

The acyclic anhydrides show two sharp bands in the carbonyl region at 1840–1800 cm^{-1} (5.44–5.56 μ) and 1780–1740 cm^{-1} (5.62–5.75 μ). Conjugation reduces the frequency of both bands by some 20 cm^{-1} to 1820–1780 cm^{-1} (5.50–5.62 μ) and 1760–1720 cm^{-1} (5.68–5.81 μ). A shift to higher frequencies is observed when the C=O is a part of a strained ring system. Succinic anhydride absorbs at 1865 cm^{-1} (5.37 μ) and 1782 cm^{-1} (5.62 μ). Despite the position of the two bands, in most cases they

are separated by approximately 60 cm^{-1} (approximately 0.2 μ).

C—O *Stretching Vibrations*

Anhydrides exhibit strong bands arising from C—O stretching. In the case of open-chain anhydrides, this absorption takes place in the region of 1170–1050 cm^{-1} (8.55–9.53 μ), whereas for cyclic anhydrides in which strain is involved, the frequency range is shifted upward to 1310–1210 cm^{-1} (7.63–8.27 μ).

Amides

All amides show a carbonyl absorption known as the amide I band. Its position is dependent upon the degree of hydrogen bonding, and thus on the physical state of the compound.

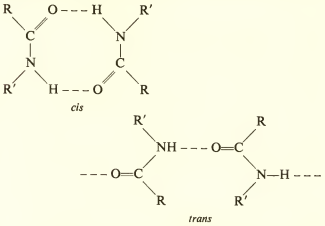
In dilute solution, primary amides show two N—H stretching bands resulting from symmetrical and asymmetrical N—H stretching. Secondary amides usually show only one band under similar conditions. As in the case of the O—H stretching, the frequency of the N—H stretching is reduced by hydrogen bonding, though to a smaller extent. Overlapping occurs between the observed position of N—H and O—H stretching frequencies so that an unequivocal differentiation of structure is sometimes impossible.

All primary and secondary amides display a band in the region of 1650–1515 cm^{-1} (6.06–6.60 μ) resulting from NH_2 or NH bending. This band is known as the amide II band; it is not displayed by lactams.

N—H *Stretching Vibrations*

In dilute solution, the primary amides show two, medium-intensity NH stretching frequencies corresponding to the asymmetrical and symmetrical vibration of the hydrogen atoms in the NH_2 group. These two bands occur near 3500 cm^{-1} (2.86 μ) and 3400 cm^{-1} (2.94 μ). The bonded NH bands of primary amides fall at lower frequencies, near 3350 cm^{-1} (2.99 μ) and 3180 cm^{-1} (3.14 μ). The bonded N—H absorption may appear as multiple bands arising from the various bonded structures such as dimers or trimers.

The spectra of secondary amides, determined in very dilute solution, show only a single free NH stretching band in the region of 3460–3420 cm^{-1} (2.89–2.93 μ). In more concentrated solutions, where bonding can occur, the free NH band diminishes and additional bands due to bonding appear at lower frequencies (longer wavelengths). The fact that more than one band results from bonding is attributed to the probability that the amide groups can bond to produce different configurations such as *cis* and *trans* configurations represented by the following structures.



The relative amounts of the various structures resulting from bonding will depend upon the concentration. Hydrogen bonding with solvent may result from the use of polar solvents.

The positions of the NH_2 and NH stretching bands can be summarized as follows:

Primary amides

Free NH_2
- 3540–3480 cm^{-1} (2.83–2.88 μ) strong
- 3420–3380 cm^{-1} (2.92–2.96 μ) strong

Bonded NH_2
- 3360–3320 cm^{-1} (2.98–3.01 μ) medium
- 3220–3180 cm^{-1} (3.11–3.15 μ) medium

Secondary amides

Free NH (*cis*)
- 3440–3420 cm^{-1} (2.91–2.93 μ) strong

Free NH (*trans*)
- 3460–3440 cm^{-1} (2.89–2.91 μ) strong

Bonded NH (*cis* and *trans*)
- 3100–3070 cm^{-1} (3.23–3.26 μ) weak

Bonded NH (*cis*)
- 3180–3140 cm^{-1} (3.15–3.19 μ) medium

Bonded NH (*trans*)
- 3330–3270 cm^{-1} (3.00–3.06 μ) medium

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C=O *Stretching Vibrations (Amide I Band)*

The location of the amide I band depends upon a number of factors: the presence or absence of substituents on the nitrogen atom; the inclusion of the amide group in a strained ring; and the physical state.

Primary amides (except acetamide, whose C=O band absorbs at 1694 cm^{-1} (5.90 μ)), have a strong C=O

absorption band (amide I band) in the region of 1650 cm^{-1} (6.06 μ) when examined in the solid phase. When the amide is examined in dilute solution, the absorption is observed at a higher frequency, 1690 cm^{-1} (5.92 μ). In concentrated solution the C=O absorption frequency is observed at some intermediate value.

Simple open chain secondary amides absorb near 1640 cm^{-1} (6.10 μ) when examined in the solid state. In dilute solution the frequency of this absorption may be raised to 1680 cm^{-1} (5.95 μ) and even to 1700 cm^{-1} (5.88 μ) in the case of the anilides. The absorption ranges apply to neutral compounds. Amides containing a free acid group, such as benzoylglycine, absorb at a lower frequency (1597 cm^{-1}, 6.27 μ) than the neutral amides.

The carbonyl frequency of tertiary amides is essentially independent of the physical state, since hydrogen bonding with another tertiary amide molecule is impossible. The C=O absorption occurs in the range of 1670–1630 cm^{-1} (5.99–6.14 μ). The absorption of tertiary amides, in which N-substitution involves a phenyl group, occurs at the higher end of this frequency range. The absorption range of tertiary amides in solution, however, is influenced by hydrogen bonding with solvents. For example, N,N-diethylacetamide absorbs at 1647 cm^{-1} (6.08 μ) in dioxane solution and at 1615 cm^{-1} (6.20 μ) in methanol.

N—H *Bending Vibrations (Amide II Band)*

All primary amides show a sharp absorption band (amide II band) at a somewhat lower frequency than the C=O absorption band. This band has an intensity of one-half to one-third of the C=O absorption band. It is observed in the solid state in the 1650–1620 cm^{-1} (6.07–6.17 μ) region and in dilute solution at 1620–1590 cm^{-1} (6.17–6.31 μ). The nature of the R group

($R—\overset{O}{\overset{\|}{C}}—NH_2$) has little effect upon the position of the amide II band.

Secondary amides, when examined in the solid state, display an amide II band in the region of 1570–1515 cm^{-1} (6.37–6.60 μ). In dilute solution, the band occurs in the 1550–1510 cm^{-1} (6.45–6.62 μ) region.

There is some question as to the origin of the amide II band. Its description as an N—H bending vibration seems an oversimplification.

Other Vibration Bands

Other bands characteristic of amide absorption can be summarized as follows:

Primary amides

1420–1400 cm^{-1} (7.04–7.14 μ) medium

Secondary amides

1305–1200 cm^{-1} (7.67–8.33 μ) medium
770–620 cm^{-1} (13.00–16.13 μ) medium

Lactams

The C=O absorption, in dilute solution, of lactams of six-membered rings or larger is near 1680 cm^{-1} (5.95 μ). Five-membered ring (γ) lactams show C=O absorption at about 1700 cm^{-1} (5.88 μ). Four-membered ring (β) lactams absorb at 1760–1730 cm^{-1} (5.68–5.78 μ). Fusion of the lactam ring to another ring generally increases the frequency by 20–50 cm^{-1} (0.07–0.17 μ).

Lactams—even those with an N—H group—do not show an amide II band. This is a useful correlation, though inexplicable on the assumption that the amide II band is an N—H bending absorption.

Out-of-plane N—H bending vibrations of lactams appear as diffuse absorption in the 700 cm^{-1} (14.3 μ) region.

Amines and Amine Salts

N—H *Stretching Vibrations*

Primary amines, examined in dilute solution, display two absorption bands in the 3500–3300 cm^{-1} (2.86–3.03 μ) region of the spectrum; these correspond to the asymmetrical and symmetrical vibrational modes, respectively, of the protons associated with the nitrogen atom. Secondary amines, under the same condition, display only one band in this region. As in the case of compounds bearing an O—H group, additional bands may appear as a result of hydrogen bonding. The shifts resulting from hydrogen bonding are to lower frequencies. The shift is not as great as observed for O—H bearing compounds, and the resulting bands are weaker and sharper. Overlapping of N—H and O—H bands occurs in this region. As the concentration is increased, not only shifting, but also the occurrence of additional peaks, may be observed for both primary and secondary amines. Tertiary amines do not absorb in this region.

In solution the amine salts (the hydrochlorides) show medium NH_2^+ stretching bands near 3380 cm^{-1} (2.96 μ) and 3280 cm^{-1} (3.05 μ). When the spectra are determined in the solid phase, medium NH_3^+ stretching bands appear in the region of 3350–3150 cm^{-1} (2.99–3.18 μ). The absorption may appear as multiple bands.

The stretching vibration of the NH_2^+ group results in strong absorption near 2700 cm^{-1} (3.70 μ). The NH^+ group absorbs with weak to medium intensity in the 2200–1800 cm^{-1} (4.55–5.56 μ) region.

N—H *Bending Vibrations*

The N—H bending vibrations occur in the region of 1650–1580 cm^{-1} (6.06–6.33 μ) for primary amines; the bands are medium to strong. Secondary amines absorb weakly in the same general region. The failure to observe bands in this region in the case of some aromatic amines probably means that the N—H bending band is overshadowed by aromatic ring vibrations occurring in this region. The N—H bending absorption is moved to somewhat higher frequencies by hydrogen bonding, but the shift is not always appreciable. Most primary amines show broad absorption in the 900–650 cm^{-1} (11.10–15.40 μ) region due to N—H bending vibrations. The position of this band is dependent upon the degree of hydrogen bonding.

The NH_3^+ group of an amine salt shows medium absorption in the regions of 1600 cm^{-1} (6.25 μ) and 1300 cm^{-1} (7.69 μ) due to asymmetrical and symmetrical bending vibrations, respectively.

C—N *Stretching Vibrations*

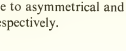
Weak absorption bands for the unconjugated C—N linkage in aliphatic amines appear in the region of 1220–1020 cm^{-1} (8.20–9.80 μ). Because of the weakness of the band and the relatively wide range of frequencies these bands are not of much significance in the correlation of molecular structure.

Characteristic strong C—N stretching in the aromatic amines has been assigned as follows.

Primary	1340–1250 cm^{-1} (7.46–8.00 μ)
Secondary	1350–1280 cm^{-1} (7.42–7.82 μ)
Tertiary	1360–1310 cm^{-1} (7.35–7.63 μ)

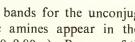
Amino Acids and Salts of Amino Acids

Amino acids are encountered in three forms: the free amino acid (zwitterion)



the hydrochloride (or other acid) salt,

the sodium (or other cation) salt,



Free primary amino acids are characterized by the following absorption (most of the work has been done with α-amino acids, but the relative positions of the amino and carboxyl groups seem to have little effect):

1. A medium, N—H stretching band at 3130–3030 cm^{-1} (3.20–3.30 μ).
2. A weak band in the 2760–2530 cm^{-1} (3.62–3.95 μ) region, and another in the 2140–2080 cm^{-1} (4.70–4.80 μ) region. These are present in most, but not all, primary amino acids and are absent when the nitrogen atom contains a substituent. The type of vibration is not known.
3. A weak N—H bending band (amino acid I band) at 1660–1610 cm^{-1} (6.03–6.22 μ), and a stronger (usually) N—H bending band (amino acid II band) at 1550–1485 cm^{-1} (6.46–6.74 μ). These bands are absent in N-substituted amino acids.
4. A medium band at about 1300 cm^{-1} (7.7 μ) of unknown origin. This is present in many, but not all, amino acids.
5. The strong ionized carboxyl absorptions at 1600–1560 cm^{-1} (6.25–6.42 μ) and (weaker) at about 1400 cm^{-1} (7.15 μ).

Hydrochloride salts of amino acids show the following pattern.

1. An unreliable N—H stretching band at 3130–3030 cm^{-1} (3.20–3.30 μ).
2. A series of moderately intense bands between 3030–2500 cm^{-1} (3.30–4.00 μ).
3. A weak N—H bending band (amino acid I band) at 1610–1590 cm^{-1} (6.21–6.29 μ) and a generally strong but variable N—H bending band at 1550–1485 cm^{-1} (6.45–6.73 μ).
4. A strong band (possible C—O stretching) at 1230–1215 cm^{-1} (8.13–8.23 μ).
5. The strong unionized carboxyl absorption at 1755–1730 cm^{-1} (5.70–5.78 μ) for α-amino acid hydrochlorides, and at 1730–1700 cm^{-1} (5.78–5.88 μ) for other amino acid hydrochlorides.

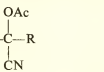
Sodium salts of amino acids show the two normal N—H stretching vibrations at 3400–3200 cm^{-1} (2.94–3.13 μ) common to other amines. The strong ionized carboxyl absorption is present at 1600–1560 cm^{-1} (6.25–6.42 μ).

Nitriles and Isonitriles

C≡N *Stretching Vibrations*

Infrared absorption by nitriles occurs in the triple-bond region of the spectrum covering the general region of 2300–2000 cm^{-1} (4.35–5.00 μ). A study of a series of nitriles places the C≡N absorption for these compounds at 2245 cm^{-1} (4.35 μ) for aliphatic nitriles; 2229 cm^{-1} (4.48 μ) for aromatic nitriles and 2220 cm^{-1} (4.50 μ) for

conjugated compounds. The band varies greatly in intensity, being strong in compounds containing C, H, and N in which the C≡N groups form a reasonable percentage of the molecules. Oxygen near or on the same carbon as the C≡N reduces the intensity. The class of compounds



shows no C≡N absorption at all. The intensity of C≡N absorption is enhanced by conjugation.

The absorption of C≡N in the same region as C≡C may make it impossible to distinguish between nitriles and acetylenes. Monosubstituted acetylenes, however, show the characteristic high frequency absorption near 3310–3300 cm^{-1} (3.02–3.03 μ) due to the C—H stretching vibration.

The isonitriles show strong absorption in the 2185–2120 cm^{-1} (4.58–4.72 μ) region.

Compounds Containing the C=N Group

C=N *Stretching Vibrations*

Absorption attributed to the C=N stretching vibration occurs between 1690–1640 cm^{-1} (5.92–6.10 μ) in open-chain systems and nonconjugated ring systems. In α,β-unsaturated oximes, it occurs at 1665–1630 cm^{-1} (6.01–6.14 μ). In cyclic systems involving α,β-unsaturation, for example, thiazoles, the band appears at 1660–1480 cm^{-1} (6.02–6.76 μ).

The intensity of the C=N absorption band is quite variable. In acyclic nonconjugated materials it may absorb more strongly than a C=C group. In cyclic systems involving conjugation, the band may vary from strong to undetectable at normal film thicknesses.

Azo Compounds

The N=N stretching vibrational frequency has not been thoroughly characterized. In some azo compounds it appears to result in absorption at 1630–1575 cm^{-1} (6.14–6.35 μ), but it is apparently absent in the tetrazoles and in some symmetrical diazo derivatives.

Heteroaromatic Compounds

C—H *Stretching Vibrations*

Pyridines, quinolines, pyrimidines, purines, and pyrroles all show C—H stretching in the general region around 3070–3020 cm^{-1} (3.26–3.32 μ), much the same as benzene.

C=C *and* C=N *Stretching Vibrations*

In the case of pyridines, two bands occur in the general region of 1650–1580 cm^{-1} (6.06–6.33 μ) and 1510–1480 cm^{-1} (6.63–6.75 μ). The higher frequency band is sometimes accompanied by another band on the high frequency side.

In the quinoline, more complex interactions between C=C and C=N are possible and three to four bands may appear in the 1600–1500 cm^{-1} (6.25–6.68 μ) region.

A study of a series of pyrimidines showed that almost all of them displayed bands in the region between 1640–1620 cm^{-1} (6.10–6.18 μ) and 1580–1560 cm^{-1} (6.33–6.41 μ).

The pyrroles with unsubstituted N show absorption at 3440–3400 cm^{-1} (2.91–2.94 μ) resulting from N—H stretching, and two bands resulting from C=C stretching absorption at about 1565 cm^{-1} (6.39 μ) and 1500 cm^{-1} (6.67 μ).

C—H *Bending Vibrations*

In pyridines, strong bands have been observed in the region at about 1200 cm^{-1} (8.33 μ) and in the 1100–1000 cm^{-1} (9.09–10.00 μ) region. Bands, typical of the number of adjacent hydrogens, occur in the region between 900–670 cm^{-1} (11.11–14.93 μ) for pyridines, and between 825–775 cm^{-1} (12.12–12.90 μ) for pyrimidines and purines.

Covalent Compounds Containing Nitrogen-Oxygen Bonds

Nitro compounds, nitrates, and nitramines contain the NO_2 group. Each of these classes of compounds shows absorption due to asymmetrical and symmetrical stretching of the NO_2 group. The absorption consists of a strong band in the 1650–1500 cm^{-1} (6.06–6.67 μ) region and another in the 1350–1250 cm^{-1} (7.42–8.00 μ) region. The exact position of the bands is dependent upon substitution and unsaturation in the vicinity of the NO_2 group.

In primary and secondary nitro compounds, the bands fall between 1565–1545 cm^{-1} (6.39–6.47 μ) and 1385–1360 cm^{-1} (7.22–7.36 μ). In tertiary nitro compounds, these bands occur at frequencies approximately 20 cm^{-1} lower than for the primary and secondary compounds. The absorption bands for α,β-unsaturated nitro

compounds appear near 1524 cm^{-1} (6.57 μ) and 1353 cm^{-1} (7.38 μ). In the α-halogenated compounds, the bands fall within the general regions of 1580–1570 cm^{-1} (6.33–6.37 μ) and 1355–1340 cm^{-1} (7.38–7.46 μ). Aromatic nitro compounds display the asymmetrical stretching band at 1550–1510 cm^{-1} (6.45–6.62 μ), and the symmetrical stretching band at 1365–1335 cm^{-1} (7.33–7.49 μ). Shifts within these regions result from hydrogen bonding. A large number of aromatic nitro-compounds show absorption near 850 cm^{-1} (11.78 μ) or 750 cm^{-1} (13.33 μ).

The limited amount of information concerning the NO stretching frequencies in covalent nitrates indicates that the asymmetrical frequency falls in the range of 1655–1610 cm^{-1} (6.04–6.21 μ), and the symmetrical stretching frequency in the region of 1300–1255 cm^{-1} (7.69–7.97 μ). Both bands are strong.

The nitramines commonly show an asymmetric stretching frequency in the 1585–1530 cm^{-1} (6.31–6.54 μ) range; the symmetrical stretching frequency occurs at 1300–1260 cm^{-1} (7.69–7.94 μ). The nitramines also show low frequency absorption in the 790–770 cm^{-1} (12.67–13.00 μ) region.

The nitrites display two very strong N=O frequency absorption bands at 1680–1650 cm^{-1} (5.95–6.06 μ) and 1625–1610 cm^{-1} (6.16–6.21 μ). These bands are attributed to the *trans* and *cis* forms of the nitrite structure. Pairs of strong bands also occur in the region between 850–750 cm^{-1} (11.76–13.33 μ) due to N—O stretching and in the range of 560–690 cm^{-1} (17.87–14.49 μ) due to O—N=O bending. The nitrite absorption bands are among the strongest observed in infrared spectra.

Difficulties have attended the assignment of absorption frequencies to nitroso compounds since the primary and secondary nitroso compounds readily convert to oximes, and the tertiary nitroso compounds dimerize.

A small amount of data is available for nitrosoamines. In solution in carbon tetrachloride the N=O frequency appears around 1450 cm^{-1} (6.90 μ). In the dimeric state this shifts to about 1310 cm^{-1} (7.63 μ).

Organic Sulfur Compounds

MERCAPTANS. The band associated with S—H stretching is generally easy to recognize because it occurs at 2600–2550 cm^{-1} (3.85–3.92 μ), a region of the spectrum which is relatively free of other absorption bands. Absorption in this frequency range is also exhibited by thioacetic acid. Intermolecular hydrogen bonding is much weaker for the S—H group as compared with O—H and N—H groups. However, a shift to 2415 cm^{-1} (4.14 μ) has been reported for the S—H absorption of the enol tautomer of ethyl thiobenzoylacetate.[18]

The S—H band is characteristically weak and may go undetected in dilute solutions or thin films. The band may be obscured by carboxyl absorption in the same general region.

SULFIDES. The stretching vibrations assigned to the C—S linkage occur in the region of 700–600 cm^{-1} (14.30–16.70 μ). The weakness of absorption and the variability of position make this band of little value in structural determination.

DISULFIDES. The S—S stretching vibration is of little value in the determination of the structure of organic compounds because it is very weak, varies in position, and falls between 500 and 400 cm^{-1} (20–25 μ), outside the range of sodium chloride optics.

COMPOUNDS CONTAINING C=S GROUP. Assignment of a position for C=S stretching bands has been difficult. The occurrence of bands at 1522 cm^{-1} (6.58 μ) and 650 cm^{-1} (15.40 μ) in the spectrum of carbon disulfide has been attributed to C=S stretching. This case, however, is unusual in that both sulfur atoms are attached to the same carbon atom.

The following assignments have been made for C=S stretching frequencies.

Thioesters	ca 1675 cm^{-1} (ca 5.97 μ)
Thioureas	1430–1130 cm^{-1} (7.00–8.85 μ)
Thioamides	ca 1120 cm^{-1} (ca 8.93 μ)
$(RS)_2C{=}S$	1060–1050 cm^{-1} (9.43–9.52 μ)
$(RO)_2C{=}S$	1235–1210 cm^{-1} (8.10–8.26 μ)
$-C{=}C-C{=}S$	1155–1140 cm^{-1} (8.65–8.77 μ)
$(Aryl)_2C{=}S$	1230–1215 cm^{-1} (8.13–8.23 μ)

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Compounds Containing Sulfur-Oxygen Bonds

Sulfoxides show a strong absorption band in the 1070–1030 cm^{-1} (9.35–9.71 μ) region when examined in dilute solution. The position of the band is very stable. Conjugation brings about little change in the observed frequency in contrast to the marked reduction in frequency of the C=O bond accompanying conjugation. Diallyl sulfoxide absorbs at 1047 cm^{-1} (9.55 μ). Phenylmethylsulfoxide and cyclohexylmethylsulfoxide both absorb at 1055 cm^{-1} (9.48 μ) in dilute solution in carbon tetrachloride.

An increase in absorption frequency on passing from the liquid phase to dilute solutions indicates some tendency to hydrogen bonding.

Bands attributed to the sulfone group (O=S=O) group

occur at 1160–1120 cm^{-1} (8.62–8.93 μ) and 1350–1300 cm^{-1} (7.41–7.70 μ). These bands are very intense and show splitting when the sulfones are examined in the

solid state. In the case of sulfonyl chlorides these bonds are shifted to higher frequencies.

The sulfonamides show two characteristic absorption bands when examined in solution. These occur in the regions of 1370–1300 cm^{-1} (7.30–7.70 μ) and 1180–1140 cm^{-1} (8.48–8.77 μ). These frequencies are lowered by 10–20 cm^{-1} in the solid phase.

Two absorption bands are characteristic of both the sulfonates and covalent sulfates. In the spectra of sulfonates these bands are observed in the 1420–1330 cm^{-1} (7.04–7.52 μ) and 1200–1145 cm^{-1} (8.33–8.73 μ) region. Similar bands at 1440–1350 cm^{-1} (6.94–7.41 μ) and 1230–1150 cm^{-1} (8.13–8.70 μ) are observed in the spectra of covalent sulfates.

Organic Halogen Compounds

The strong characteristic absorptions, which are assigned to organic compounds containing halogen, arise from the stretching vibrations of the carbon to halogen bond. The frequency at which the vibration occurs is influenced by neighboring groups in the molecules.

The C—F vibration is most easily influenced by interactions because of the low mass of the fluorine atom. Fluorine-containing compounds absorb strongly over a wide region between 1400–1000 cm^{-1} (7.15–10.00 μ). The following assignments have been made for fluorinated compounds.

Monofluorinated
1110–1000 cm^{-1} (9.01–10.00 μ) 1 strong band
Difluorinated
1250–1050 cm^{-1} (8.00–9.50 μ) 2 strong bands
Polyfluorinated
1400–1100 cm^{-1} (7.14–9.10 μ) multiple strong bands

The C—Cl stretching frequency for monochlorinated compounds falls into the 750–700 cm^{-1} (13.33–14.29 μ) region of the spectrum. In solution, a second band is observed near 650 cm^{-1} (15.40 μ). When several chlorine atoms are connected to a single carbon atom, the absorption frequency is increased; for example, carbon tetrachloride shows an intense band at 797 cm^{-1} (12.55 μ). In polychlorinated compounds which show an intense fundamental absorption band, the first overtone may be observed in the region around 1500 cm^{-1} (6.66 μ). Brominated compounds show two bands in the 600–500 cm^{-1} (16.67–20.00 μ) region. Alkyl iodides absorb in the general region of 500 cm^{-1} (20.00 μ).

References

1. Jones, R. N., and C. Sandorfy, "The Application of Infrared and Raman Spectrometry to the Elucidation of Molecular Structure," Chapter IV, Vol. IX, in A. Weissberger, *Technique of Organic Chemistry*, Interscience, New York, 1956, pp. 247–580.
2. Miller, F. A., "Applications of Infrared and Ultraviolet Spectra to Organic Chemistry," Vol. III, in H. Gilman, *Organic Chemistry, An Advanced Treatise*, John Wiley, New York, 1953, pp. 122–77.
3. Bellamy, L. J., *The Infra-red Spectra of Complex Organic Molecules*, John Wiley, New York 2nd ed., 1958.
4. Cross, A. D., *Introduction to Practical Infra-red Spectroscopy*, Butterworths Scientific Publications, London, 1960.
5. Randall, H. M., R. G. Fowler, N. Fuson, and J. R. Dangl, *Infrared Determination of Organic Structures*, D. Van Nostrand, New York, 1949.
6. Williams, V. Z., "Infrared Instrumentation and Techniques," *Rev. Sci. Instruments* **19**, 135–78 (1948).
7. Herzberg, G., *Infrared and Raman Spectrum of Polyatomic Molecules*, D. Van Nostrand, New York, 1945. Theory.
8. Barnes, R. B., R. C. Gore, U. Liddel, and V. Z. Williams, *Infrared Spectroscopy*, Reinhold, New York, 1944.
9. Sutherland, G. B. B. M., *Infrared and Raman Spectra*, Methuen, London, 1935. Theory.
10. Bauman, R. P., *Absorption Spectroscopy*, John Wiley, New York, 1962.
11. "Catalog of Infrared Spectrograms," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Penn.
12. Randall, H. M., R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand, New York, 1943.
13. *Catalog of Infrared Spectrograms*, Samuel P. Sadtler, Philadelphia, Penn.
14. *Catalog of Infrared Spectral Data*, Manufacturing Chemists Association Research Project, Chemical and Petroleum Research Laboratories, Carnegie Institute of Technology, Pittsburgh, Penn., to June 30, 1960; Chemical Thermodynamics Properties Center, Agriculture and Mechanical College of Texas, College Station, Tex., from July 1, 1960.
15. *An Index of Published Infra-Red Spectra*, M. B. B. Thomas, ed., Vols. I and II, British Information Service, 45 Rockefeller Plaza, New York, 1960. Complete to 1957. Gives literature references to spectra, lists state, absorption range, and optics.
16. Szymanski, H. A., *Infrared Band Handbook*, Plenum, New York, 1962.
17. "Spectrometry Nomenclature," *Anal. Chem.*, **33**, 1968 (1961.)
18. Reyes, Z., and R. M. Silverstein, *J. Am. Chem. Soc.*, **80**, 6367 (1958).
19. *Documentation of Molecular Spectroscopy* (*DMS*), Butterworths Scientific Publications, London; and Verlag Chemie GMBH, Weinheim/Bergstrasse, West Germany, in cooperation with the Infrared Absorption Data Joint Committee, London, and the Institut fur Spectrochemie und Angewandte Spectroskopie, Dortmund. Spectra are presented on coded cards. Coded cards containing abstracts of articles relating to infrared spectrometry are also issued.

CHAPTER FOUR

Nuclear Magnetic Resonance Spectrometry

INTRODUCTION AND THEORY

Nuclear magnetic resonance (NMR) spectrometry is basically another form of absorption spectrometry, akin to infrared or ultraviolet spectrometry. Under appropriate conditions a sample can absorb electromagnetic radiation in the radio-frequency region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. This discussion will be limited to proton NMR spectra.

Whereas the organic chemist has dealt for some time on quite familiar terms with electrons, he has generally assumed a posture of mingled foreboding and bemusement toward the arcana of nuclear phenomena. In view of the rapid development of nuclear magnetic resonance as a tool for the organic chemist whose commitments range from mechanisms to recipes, he can reasonably expect some guidance in his approach to a new field. This guidance has been forthcoming within the past few years in the form of excellent books and reviews. For a further nonmathematical introduction to nuclear magnetic resonance, the organic chemist is urged to read the lucid brief monographs by Jackman[1] and by Roberts.[2] The present account will suffice for

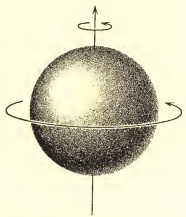


Fig. 1. Spinning charge in Nucleus generates magnetic dipole.

the immediate limited objective, that is, identification of organic compounds in conjunction with other spectrometric information.

We begin by describing some magnetic properties of nuclei. All nuclei carry a charge. In some nuclei this charge circulates or "spins" on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Figure 1). The angular momentum of the spinning charge can be described in terms of spin numbers I; these numbers have values of 0, 1/2, 1, 3/2, and so forth. ($I = 0$ denotes no spin). The intrinsic magnitude of the generated dipole is expressed in terms of a nuclear magnetic moment, μ.

In general, nuclei with an even number of protons and an even number of neutrons have a spin number I of zero. Both C^{12} and O^{16} fall in this category; they do not give rise to an NMR signal or interfere with a proton NMR signal.

Several nuclei (H^1, F^{19}, C^{13}, and P^{31}) have spin number I of 1/2. These nuclei possess a uniform spherical charge distribution (Figure 1), and are characterized by having either an odd number of protons or an odd number of neutrons.

Nuclei with spin number I of 1 or higher have a nonspherical charge distribution; this asymmetry is described by an electrical quadrupole moment which, as we shall see later, affects the relaxation time and, thus, the coupling with neighboring nuclei. N^{14} and H^2 have a spin number I of 1. B^{11}, Cl^{35}, Cl^{37}, Br^{79}, and Br^{81} are examples of nuclei with $N = 3/2$.

The spin number I determines the number of orientations a nucleus may assume in an external uniform magnetic field in accordance with the formula $2I + 1$. We shall be concerned primarily with the proton whose spin number I is 1/2. Thus, the proton has two orientations in an applied uniform magnetic field: parallel with the applied field (aligned with the field) or antiparallel (aligned against the field). The former is the low-energy (stable) state, the latter, the high-energy (unstable) state. The energy levels are a function of the magnitude of the nuclear magnetic moments, μ, and the strength of the applied external magnetic field, H_0.

Two energy levels for the proton having been established, it should now be possible to introduce quanta of energy, $h\nu$ (h is Planck's constant; ν is the frequency of electromagnetic radiation) such that the parallel orientation (low-energy state) can be flipped to the antiparallel orientation (high-energy state) in a magnetic field of given strength H_0. The fundamental NMR equation correlating electromagnetic frequency with magnetic field strength is

$$\nu = \gamma H_0/2\pi$$

The constant γ is called the magnetogyric (or more commonly but less properly, gyromagnetic) ratio and is a fundamental nuclear constant.

The bald statement made earlier that nuclear magnetic resonance spectrometry is akin to other forms of absorption spectrometry may now seem somewhat more plausible. The problem now is how to inject electromagnetic energy into protons aligned in a magnetic field so as to flip the proton spin into a higher energy level, and how to measure the energy thus absorbed. Before we describe the instrumentation, we have to consider one peculiarity of a small magnet spinning in an external magnetic field: The axis of the small magnet (the proton) will precess about the axis of the external magnetic field in the same manner in which a spinning gyroscope precesses under the influence of gravity. The precessional angular velocity, ω_0 is equal to the product of the magnetogyric ratio, γ and the strength of the applied magnetic field H_0.

$$\omega_0 = \gamma H_0$$

We recall from the fundamental NMR equation that

$$\gamma H_0 = 2\pi\nu$$

Therefore,

$$\omega_0 = 2\pi\nu$$

This means that if we can introduce the same frequency, equal to γH_0 (the energy required to flip a proton), we shall be precisely attuned to the precessional angular velocity. Or to put it another way, the inserted frequency will be *in resonance* with the precessional frequency. The energy of the inserted frequency can thus be absorbed by the nucleus and, given the proper geometry, the nucleus can be caused to flip. This involves a frequency of 60 megacycles per second at a magnetic field H_0 of 14,092 gauss for the proton (or any other desired combination in the same ratio).

We are now in a position to arrange the geometry for a nuclear magnetic-resonance experiment. We subject the protons to a powerful uniform magnetic field. The protons are now aligned parallel with the field and are precessing about the axis of the applied magnetic field. Because of thermal disorder, actually only a small excess

of the total population of protons is properly aligned, but this excess is sufficient. The electromagnetic frequency is applied in such a way that its magnetic component H_1 is at right angles to the main magnetic field H_0 and is rotating with the precessing proton. An oscillator coil whose axis is at right angles to the axis of the main magnetic field H_0 will generate a linear oscillating magnetic field H_1 along the direction of the coil axis as shown in Figure 2. A linear oscillating magnetic field can be resolved into two components rotating in opposite directions. One of these components is rotating in the same direction as the precessional orbit of the nuclear magnetic dipole (the proton); the oppositely rotating component of H_1 is disregarded. If H_0 is held constant and the oscillator frequency is increased, the angular velocity of the component of rotating magnetic field H_1 will increase until it is equal to (in resonance with) the angular velocity ω_0 of the precessing proton. At this point, energy is absorbed, the nucleus flips to its higher energy level, and the recorder shows a peak. In actual practice, the oscillator frequency is constant, and H_0 is swept over a narrow range.

There is one further complication. We need some mechanism to return the nucleus to its lower-energy state. In the absence of such a mechanism, all of the small excess population of nuclei in the lower-energy state will be raised to the higher-energy state, and no more energy will be absorbed. Fortunately, there exists a mechanism whereby the nucleus in the higher energy state can lose energy to its environment and thus return to its lower energy state. The mechanism is called a spin-lattice, or longitudinal, relaxation process and involves transfer of energy from the nucleus in its high-energy state to the molecular lattice. Its efficiency is described as the time T_1 taken for the transfer. An efficient relaxation process involves a short time T_1 and results in broadening of the absorption peak. In liquids and gases, the time T_1 is of the proper duration to produce a peak of usable width. In solids, this mechanism is not effective; T_1 is therefore very long, and in the absence of any other effects, a crystalline solid would show extremely narrow lines. There is another effect, called spin-spin or transverse relaxation, operative in solids. This involves transfer of energy from one high-energy nucleus to another. There is no net loss of energy, but the spread of energy among the nuclei concerned results in line broadening. In fact, this latter mechanism causes line broadening of such magnitude as to render NMR spectra of solids of little interest to the organic chemist.

We can now consider very briefly the instrumentation necessary to obtain a nuclear magnetic resonance spectrum.

APPARATUS

A high-resolution (defined later) nuclear magnetic-resonance instrument is commercially available from only one source in this country. Varian Associates, Palo Alto, California, manufactures a versatile research instrument (HR60) which will operate at a frequency of 60 megacycles per second for protons, and at the proper combination of frequencies and magnetic fields for F^{19}, B^{11}, C^{13}, and P^{31}. Temperature control is available over a wide range. The cost with accessories, including recorder and integrator, is in the neighborhood of $45,000. The HR100 is a 100-megacycle instrument and is now available at about $50,000. Varian offers its A60 model at about $23,000. This is a 60-megacycle instrument and is limited to proton work. Its stability is such that a spectrum can be obtained on a precalibrated chart. Both the Perkin-Elmer Corporation, Norwalk, Connecticut and Trub, Tauber and Company, S.A.,

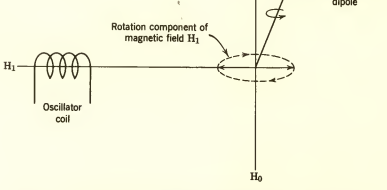


Fig. 2. Oscillator generates rotating component of magnetic field H_1.

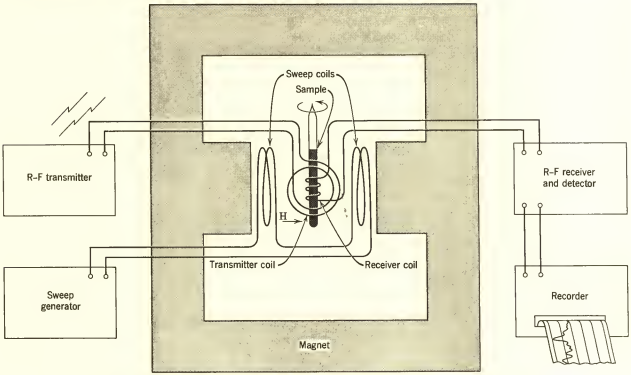


Fig. 3. Schematic diagram of an NMR Spectrometer. (Courtesy of Varian Associates, Palo Alto, Calif.)

Zurich, Switzerland, market high-resolution NMR instruments in Europe. The Perkin-Elmer instrument operates at 40 megacycles for protons, and the Trub, Tauber instrument at 25 megacycles.

A schematic diagram of an NMR spectrometer is shown in Figure 3. The instrument can be described in terms of the following components:

1. A strong magnet whose homogeneous field can be varied continuously and precisely over a relatively narrow range. This is accomplished by means of the sweep generator.
2. A radio-frequency oscillator.
3. A radio-frequency receiver.
4. A recorder, calibrator, and integrator.
5. A sample holder which positions the sample relative to the main magnetic field, the transmitter coil and the receiver coil. The sample holder also spins the sample to increase the apparent homogeneity of the magnetic field.

The sample, a liquid or a solution in a suitable solvent, is contained in a 5 mm O.D. glass tube. Ordinarily about 0.4 ml of a liquid or somewhere between 10 to 50 mg of a solid dissolved in 0.4 ml of a solvent is used, By using nylon plugs to cut down on dead space—that is, by restricting the sample to the region of the receiver coil—the volume of liquid or solution can be reduced to about 0.2 ml. A specially designed spherical cavity[8] made of nylon reduces the volume to about 0.025 ml, so that samples of about 1 mg can be run in solution; however, the spectrum suffers from a rather high noise level.

Useful solvents for proton spectra are carbon tetrachloride and carbon disulfide (no solvent peaks); acetone, acetonitrile, chloroform, benzene, cyclohexane, dimethyl sulfoxide, dioxane, and water (one solvent peak); and the following deuterated solvents: chloroform, benzene, acetone, dimethylsulfoxide, and water (no solvent peaks).

Details of operation will not be described. Suffice to say that with the radio frequency oscillator set at 60 megacycles per second, the sweep generator periodically sweeps the main magnetic field in the immediate vicinity of 14,092 gauss. For protons, the range of sweep is of the order of 1000 cycles per second or so. Calibration of chemical shifts is in dimensionless units (parts per million δ, or tau values τ), from a reference marker (vide infra). Peak areas are measured by the integrator, which, on the A-60 spectrum, superimpose a series of steps on the absorption peaks; the step heights are proportional to the number of protons under the respective peaks. As will be noted in Chapter 6, proton counting with the integrator is extremely useful for identification. Peaks hidden under other peaks can thus be detected. Proton counting is often a useful method for determining sample purity.

CHEMICAL SHIFT

Thus far, we have obtained a simple peak from the interaction of radio-frequency and a strong magnetic

field on a proton in accordance with the basic NMR equation in which γ, the magnetogyric ratio, is an intrinsic property of the nucleus ($\nu = \gamma H_0/2\pi$). The peak area (measured by the integrator) is proportional to the number of protons it represents. Fortunately, the situation is not quite so simple. The nucleus is shielded to a small extent by its electron cloud whose density varies with the environment. This variation gives rise to chemical shifts within the range of 1000 cycles per second or so in a magnetic field corresponding to 60×10^6 cycles per second. The ability to discriminate among the chemical shifts describes high resolution NMR spectrometry. Actual measurements are made with an accuracy of about a cycle per second relative to a reference.

Electrons under the influence of a magnetic field will circulate, and, in circulating, will generate their own magnetic field opposing the applied field; hence, the shielding effect. This effect accounts for the diamagnetism exhibited by all organic materials. In the case of materials with an unpaired electron, the paramagnetism associated with the net electron spin overrides the diamagnetism of the circulating, paired electrons. The degree of shielding depends on the density of the circulating electrons, and, as a first, very rough approximation, the degree of shielding of a proton on a carbon atom will depend on the inductive effect of other groups attached to the carbon atom. These are small effects; as we pointed out, we are talking about shifts of parts per million in relation to a standard reference. The most generally useful reference is tetramethylsilane ($(CH_3)_4Si$. In this case, chemical intuition is a dependable guide; it tells us that the electron density around the protons of tetramethylsilane (silicon is less electronegative than carbon) will be higher than the density around methyl chloride protons, for example. The protons of tetramethylsilane will be more highly shielded than those of methyl chloride, or, to put it another way, the methyl chloride protons are deshielded relative to the tetramethylsilane protons. Let us set up a scale of chemical shifts in dilute solution (to avoid polar solvent effects as much as possible, we use carbon tetrachloride as a solvent), and set tetramethylsilane at 0.00 cycle per second at the right-hand end of the scale. The peak for the methyl chloride protons will appear at 180 cycles per second to the left—at a lower field. Chemical shifts are expressed in dimensionless units δ obtained by dividing the distance of the shifts from the reference, in cycles per second, by the applied frequency and multiplying by 10^6. In the case of methyl chloride (at 60 megacycles)

$$\delta = \frac{180 \times 10^6}{60 \times 10^6} = 3.00 \text{ parts per million}$$

This scheme has been criticized because values of δ increase in the downfield direction; the rejoinder is that these are really negative numbers. The other commonly used system assigns a value of 10.00 for tetramethylsilane, and describes chemical shifts in terms of τ values

$$\tau = 10.00 - \delta$$

It should be noted that δ is treated as a positive number. We shall make our assignments in both δ and τ values.

We could make a number of good guesses as to chemical shifts using concepts of electronegativity and proton acidity. For example, the following values are reasonable on these grounds:

	δ	τ
$(CH_3)_2O$	3.27	6.73
CH_3F	4.30	5.70
RCOOH	10.8	−0.8

But finding the protons of acetylene at δ 2.35, τ 7.65, that is, more shielded than olefinic protons (δ 4.60, τ 5.40) is unsettling. And finding the aldehydic proton of acetaldehyde at δ 9.97, τ 0.03 definitely calls for some augmentation of chemical intuition. We shall use diamagnetic anisotropy to explain these and other apparent anomalies, such as the unexpectedly large deshielding effect of the benzene ring (benzene protons δ 7.27, τ 2.73) and the high field position in very dilute solution for the hydroxylic proton of alcohols, which lies in the same general range as ordinary methyl and methylene protons.

Let us begin with acetylene. The molecule is linear, and the triple bond is symmetrical about the axis. If this axis is aligned with the applied magnetic field, the π-electrons of the bond can circulate at right angles to the applied field, thus inducing their own magnetic field opposing the applied field. Since the protons lie along the magnetic axis, the magnetic lines of force induced by the circulating electrons will act to shield the protons (Figure 4) and the NMR peak is found further upfield than chemical intuition would predict.

This effect is called diamagnetic anisotropy; it depends on the orientation of the bond with respect to the applied magnetic field. Similar arguments can be adduced to rationalize the unexpected low field position of the aldehydic proton. In this case, the effect of the applied magnetic field is greatest along the transverse axis of the C=O bond (that is, in the plane of the page). The geometry, as can be seen in Figure 5, is such that the aldehydic proton, which is in the plane of the page, lies in the deshielding portion of the induced magnetic field. The same argument can be used to account for at least part of the rather large amount of deshielding of olefinic protons.

The so-called "ring-current effect" is another example of diamagnetic anisotropy and accounts for the large deshielding of benzene ring protons. Figure 6 shows this

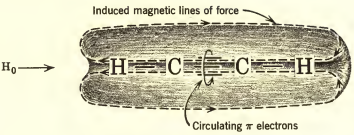


Fig. 4. Shielding of acetylenic protons.

effect. It also indicates that a proton held directly above or below the ring should be shielded. This has actually been found to be the case for some of the methylene protons in 1,4-polymethylenebenzenes.

If effects due to hydrogen bonding are eliminated by working in very dilute nonpolar solvents or in the vapor phase, there is not much variation in the positions of protons directly attached to oxygen, nitrogen, or halogens. In fact, they are all close to methyl signals in paraffins. This is apparently attributable to magnetic anisotropy of the bond between the hetero atom and the hydrogen atom.

The widely published spectrum of ethyl alcohol has led to a common misconception that the hydroxylic proton is far downfield. This is true of neat ethanol. The position of the absorption peak of a hydroxylic proton is a function of hydrogen bonding, and in a dilute solution of an alcohol in carbon tetrachloride, for example, the hydroxylic proton peak may often be buried in the alkyl proton peaks. The phenolic proton position also depends on concentration and on the solvent. These effects are used to study hydrogen bonding. It is possible to distinguish between intermolecular and intramolecular bonding, since both are temperature dependent (upfield shift on warming), but only intermolecular bonds are shifted upfield on dilution. We see, in effect, an equilibrium position between bonded and nonbonded protons with very rapid interchange of protons. Warming causes an increased concentration of the nonbonded protons, and the equilibrium position is shifted upfield. Dilution likewise causes a higher concentration of unbounded protons, provided they are intermolecular bonds.

The organic chemist will accept the foregoing crude pictorial representation as a mnemonic device and as a basis for extrapolations. He will then proceed to use NMR spectrometry as he uses infrared—as an empirical tool. We have, therefore, summarized some chemical shift data as Appendix A; a set of shielding constants and a chart for disubstituted methylene groups as Appendix B; and chemical shifts of protons subject to hydrogen bonding effects as Appendix C. These data are presented as δ and τ values. To change to cycles per second, the δ value is multiplied by the frequency in megacycles per second. For example, a δ value of 3.00 for methyl chloride would be equivalent to 120 cycles per second on a 40-megacycle instrument or to 180 cycles per second on a 60-megacycle instrument. It is important to realize that the chemical shift in cycles per second is directly proportional to the strength of the applied field H_0 and, therefore to the electromagnetic frequency. This is understandable because the chemical shift is dependent on the diamagnetic shielding induced by H_0. Given adequate homogeneity, a strong magnetic field is advantageous in spreading out the chemical shifts and thus separating them from splits due to *spin-spin coupling*, our next topic.

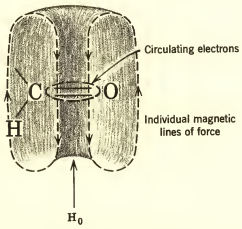


Fig. 5. Deshielding of aldehydic proton.

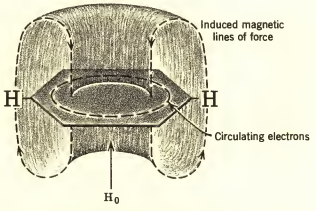


Fig. 6. Ring current effects in benzene.

SPIN-SPIN COUPLING

We have obtained a series of peaks representing protons in different chemical environments; each peak area is proportional to the number of protons it represents. This achievement alone furnishes considerable information. We have now to consider one further refinement, spin-spin coupling. This can be described as the indirect coupling of proton spins through the intervening bonding electrons. Very briefly, it occurs because there is some tendency for a bonding electron to pair its spin with the spin of the nearest proton; the spin of a bonding electron, having been thus influenced, the electron will affect the spin of the other bonding electron and so on through to the next proton as in Figure 7. The two spin possibilities (with or against the applied field) of a proton are denoted by arrows through the protons pointing up or down. Coupling is ordinarily not important beyond the three bonds illustrated in Figure 7 unless there is some bond delocalization, as in aromatic or olefinic bonds.

Suppose the two protons shown in Figure 7 are in very different chemical environments from one another. Each will give rise to a peak depending on its chemical shift and the peaks will be quite widely separated. But the spin of each proton is affected slightly by the other proton in two ways through the intervening electrons so that each peak appears as a doublet under good resolution (Figure 8a). The distance between the peaks (or possibly peaklets) of a doublet is proportional to the effectiveness of the coupling, and is denoted by a coupling constant J which is independent of the applied magnetic field H_0. Whereas chemical shifts can range over about 1000 cycles per second, coupling constants between protons rarely exceed 20 cycles. So long as the chemical shift difference is much larger than the coupling constant ($\delta_2 - \delta_1/J$ is greater than about 10), the simple pattern of two doublets appears. As the chemical shift difference becomes smaller and the spin-spin coupling constant becomes larger, the peaks approach one another; the inner two peaks increase in intensity and the outer two peaks decrease (Figure 8b).

When the chemical shift difference becomes zero, the peaks coalesce to give a single peak—that is, the protons are equivalent. (Chemically equivalent protons do spin-spin couple with one another but the transitions are forbidden.) A further point to be noted is the obvious one that the spacing between the multiplets is the same in one proton as it is in other protons coupled to it. The dependence of chemical shift on the applied magnetic field and the independence of the spin-spin coupling afford a method of distinguishing between them. The spectrum is merely run at two different applied magnetic fields; this is possible on the HR60 model but not on the A-60. Chemical shifts are also solvent dependent, but J values are not affected by change of solvent.

Let us now look at the next stage in complexity of

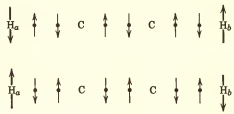


Fig. 7. Spin-spin coupling of protons through the bonding electrons.

spin-spin coupling. Consider the system—HC—CH_2—in which the single methine proton is in a very different chemical environment from the two methylene protons. As before, we shall see two peaks widely separated, and now the peak areas are in the ratio of 1 : 2. The methine proton will couple with the methylene protons and split the methylene proton peak into a symmetrical doublet, as explained above. The two methylene protons will split the methine proton peak into a triplet because the following combinations of proton spins exist in the two methylene protons (a and b).

$$\begin{array}{cccc} \uparrow\uparrow & \uparrow\downarrow & \downarrow\uparrow & \downarrow\downarrow \\ a\,b & a\,b & a\,b & a\,b \end{array}$$

The middle pairs are equivalent, and the intensities of each peak of the triplet are therefore in the ratio 1 : 2 : 1 (Figure 9).

A generalized set of rules can now be formulated on the basis of what we have just observed. Thus far, we have assumed all protons on the same carbon atom to be equivalent. This is only true if there is no appreciable barrier to rotation around the carbon bonds.

1. Splitting of a proton peak is done by neighboring protons, and the multiplicity of the split is determined by the number of these protons. Thus, one proton causes a doublet, and two equivalent protons cause a triplet. The multiplicity, then is $n + 1$, n being the number of neighboring equivalent protons. The more general formula which covers all equivalent nuclei is $2nI + 1$, I being the spin number.

2. The relative intensities of the peaks of a multiplet also depend on n. We have seen that doublet ($n = 1$) peaks are in the ratio 1 : 1, and triplet peaks are in the ratio 1 : 2 : 1. Quadruplets are in the ratio 1 : 3 : 3 : 1. The general formula is $(a + b)^n$; when this is expanded to the desired value of n, the coefficients will give the relative intensities.

Following Pople,[3] we shall designate nonequivalent protons separated by a small chemical shift with the letters A, B, and C, and protons separated from these by a large chemical shift ($\delta_2 - \delta_1/J > 10$) with the letters X, Y, and Z . The number of protons in each group is denoted by a subscript number. Thus, the first case we examined (Figure 8a) is an AX system. The second case

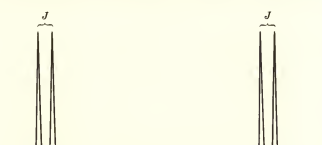


Fig. 8a. Spin-spin coupling between two protons with very different chemical shifts.

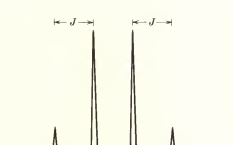


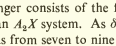
Fig. 8b. Spin-spin coupling between protons with a smaller difference in chemical shifts and a larger J value.

(Figure 8b) is an AB system, and the third case (Figure 9) is an A_2X system. A useful table of spin-spin constant values (J values) is presented in Appendix D. Fluorine nuclei also couple with protons; the rules are the same as for H—H coupling, but the J values are usually somewhat larger. Several J_{HF} values are included in Appendix D.

A system of three nonequivalent protons each separated by a large chemical shift can be designated an AMX system (see Compound 6-6). An example of a A_2M_2X system is given by Compound 6-7.

In general, we can analyze A_mX_n and $A_mM_nX_o$ (m, n, o are integers) types merely by inspection and the use of a set of dividers. The AB system is also obvious. But an A_2B system no longer consists of the five lines that are characteristic for an A_2X system. As $\delta_2 - \delta_1/J$ becomes smaller, as many as from seven to nine lines may appear as a result of second-order splitting.

A system may have more than a single coupling constant. An example is furnished on p. 79 of this chapter and in several of the compounds in Chapters 6, 7, and 8. The following examples will further illustrate the classification system and will perhaps answer some commonly raised questions. (R and R^1 represent functional groups.)



AX or AB

$J_{\alpha\beta}$

Ideally 2 doublets

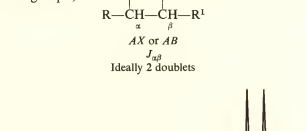
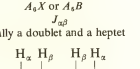


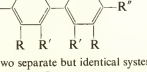
Fig. 9. Spin-spin coupling between CH and CH_2 with very different chemical shifts.



A_2X_2 or A_2B_2

$J_{\alpha\beta}$

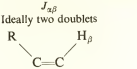
Ideally 2 triplets



A_4X or A_4B

$J_{\alpha\beta}$

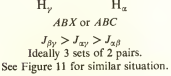
Ideally a doublet and a quintet



A_6X or A_6B

$J_{\alpha\beta}$

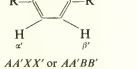
Ideally a doublet and a heptet



AX or AB (two separate but identical systems)

$J_{\alpha\beta}$

Ideally two doublets

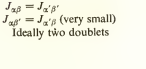


ABX or ABC

$J_{\beta\gamma} > J_{\alpha\gamma} > J_{\alpha\beta}$

Ideally 3 sets of 2 pairs.

See Figure 11 for similar situation.



$AA'XX'$ or $AA'BB'$

$J_{\alpha\beta} = J_{\alpha'\beta'}$

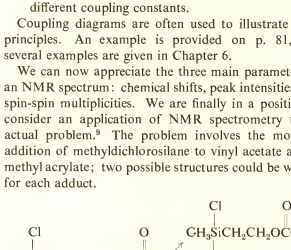
$J_{\alpha\beta'} = J_{\alpha'\beta}$ (very small)

Ideally two doublets

When $J_{a\beta'} = J_{x'\beta} = 0$, the system is AX or AB. The "prime" designation is used to differentiate two identical protons (that is, with the same chemical shift) which are coupled to another proton by different coupling constants.

Coupling diagrams are often used to illustrate these principles. An example is provided on p. 81, and several examples are given in Chapter 6.

We can now appreciate the three main parameters of an NMR spectrum: chemical shifts, peak intensities, and spin-spin multiplicities. We are finally in a position to consider an application of NMR spectrometry to an actual problem.[9] The problem involves the mode of addition of methyldichlorosilane to vinyl acetate and to methyl acrylate; two possible structures could be written for each adduct.



At the time these spectra (Figure 10) were run, the available high resolution NMR spectrometer was operated at 30 megacycles per second and 7050 gauss; the reference was benzene, and the liquid samples were run neat. It may be an instructive exercise for the student to recalculate shift positions at 60 megacycles per second referred to tetramethylsilane.

Simply on the basis of the proton spin-spin interactions, it is clear that the structures of the two adducts are as shown in Figure 10. The two-triplet peaks a and c (of equal area) of the vinyl acetate adduct are assignable to the $—CH_2CH_2—$ structure (A_2X_2); the doublet, quartet groupings g and f (with the areas in the ratio 3 : 1) of the methyl acrylate adduct clearly show the presence of the

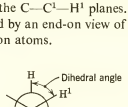
—CH— structure (A_3X). The fact that h lies at a higher field than a and that b lies at a higher field than f conforms to the general pattern of NMR spectra wherein the more highly protonated of two otherwise similar groups shows resonance at a higher field. As features of interest, it should be noted that the CH_3 groups on *Si* (*d* and *e*) are highly shielded singlets; the CH_3 group on O(*h*) is a strongly deshielded singlet, and the CH_3 group adjacent to C═O is a moderately deshielded singlet.

More Complex Spin-Spin Couplings

The clean-cut spin-spin couplings already depicted are rather rare examples. In fact, when $\delta_2 - \delta_1/J$ is small and when more than one J value is involved, the situation deteriorates to gross distortions caused by second order effects. A nice example of a system that is no longer simple but can still be analyzed by inspection is represented by styrene oxide (Figure 11). The figure and the interpretation closely follow Roberts.[10] The system is ABX and there are three coupling constants. The α-proton is the X component since it is shifted downfield by the benzene ring. Only the side chain protons are considered. Because of the fixed geometry, H_β and $H_{\beta'}$ are not chemically equivalent nor do they have the same coupling to H_α. $J_{\alpha\beta} > J_{\alpha\beta'}$ in accordance with the rule of thumb that *trans* coupling is about twice as effective as *cis* coupling in many rigid systems. Ignoring coupling, we would have a simple three-line proton spectrum as shown at the top of Figure 11. We then show the α-proton split by the β-proton ($J_{\alpha\beta}$), and each line split again by the β′-proton ($J_{\alpha\beta'}$). This gives us a multiplet of two pairs of peaks of roughly equal size. The β-proton is split by the β′-proton ($J_{\beta\beta'}$), then in turn by the α-proton ($J_{\alpha\beta}$) to give another multiplet of two pairs. The β′-proton is split by the β-proton ($J_{\beta\beta'}$) and by the α-proton ($J_{\alpha\beta'}$) to give the third multiplet. The distortion on the right hand side of the spectrum is a result of the small shift distance between H_β and $H_{\beta'}$.

The student will doubtless make the distinction between a 1,3,3,1 quartet caused by three equivalent protons, and the 1,1,1,1 appearance of two pairs brought about by splitting of two nonequivalent protons.

Karplus[11] has pointed out the dependence of J on bond angles. For geminate protons  , J decreases from about 20 cycles per second at a bond angle of 105° to zero at a bond angle of about 125°. In the case of coupling between protons on vicinal carbons[12], J decreases almost linearly from about 8 at 0° to about 0 at 90°, and then increases to about 10 at 180°. The angle referred to here is the dihedral angle between the H—C—C^1 and the C—C^1—H^1 planes. This bond angle can be visualized by an end-on view of the bond between the vicinal carbon atoms.



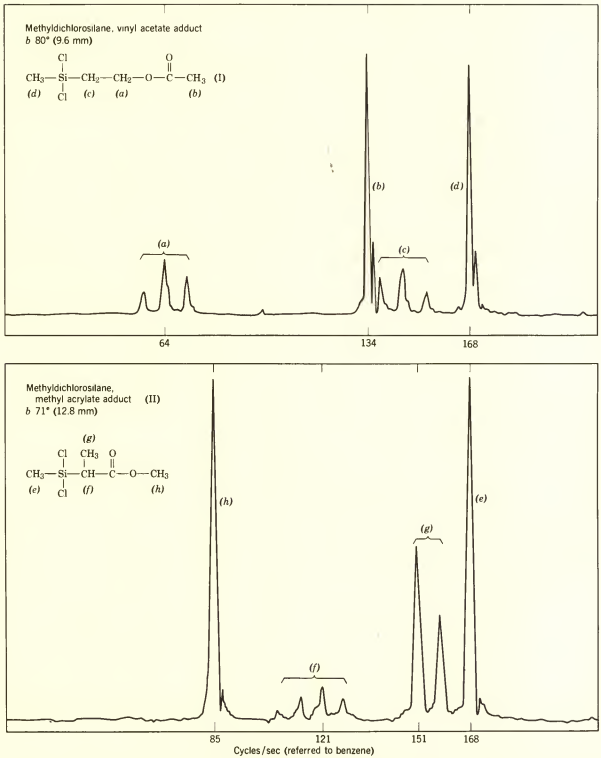


Fig. 10. Proton nuclear magnetic resonance spectra of methyldichlorosilane adducts. Samples in 5 mm tubes. (Varian Associates High Resolution Spectrometer (V-4300B) at 30 megacycles and 7050 gauss.)

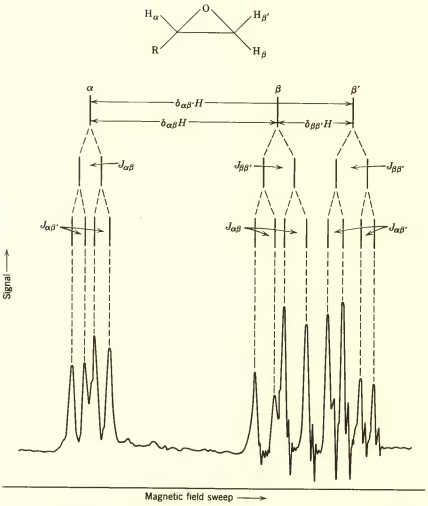


Fig. 11. Proton NMR spectrum of styrene oxide at 40 megacycles illustrating interaction between three nonequivalent protons. The resonance of the phenyl protons is off-scale on the left. (From Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York. Used by permission.)

We shall not deal with very involved spin-spin couplings. There are three approaches to the problem posed by complicated systems:

1. Quantum mechanical calculations[13]
2. Substitution of deuterium for hydrogen
3. Double-irradiation technique

Deuterium has a spin number I of 1, and we would expect that its splitting would be more complex than that of protons. However, its coupling constant with protons is very small (about one-seventh of proton-proton coupling constants), and, therefore, only single peaks (slightly broadened) result.

The double-irradiation technique, known also as double-resonance or spin-decoupling, offers the greatest potentiality of relief from complex spin-spin couplings. Spin-spin coupling involves a time factor; the proton (or other nucleus) responsible for the splitting must exist in a given spin state for a finite length of time. Or to look at the situation from the point of view of the proton whose spin is being split, this proton must be able to see distinct spin states of the splitter proton. If the proton being split can see the spin states of the splitter proton changing somewhat more rapidly, its own multiplicity will become less distinct and this multiplicity will degenerate into a broad peak. When the spin states of the splitter proton are changing very rapidly, the viewing proton now sees one equivalent state, and a sharp peak results. The double-irradiation technique is simply a method of irradiating the splitter nucleus specifically with its resonance frequency, thus artificially "stirring-up" its spin states. This has been done with protons.[14] At this writing, no double-irradiating device is commercially available.*

This technique has also been applied to "stir up" the spin states of N^{14} and, thus, decouple it from an attached proton, as in pyrrole. The nitrogen nucleus has a spin

* A decoupler for unlike nuclei is available from Nuclear Magnetic Resonance Specialties, 305 Kingston Drive, Pittsburgh 35, Pa. Varian Associates markets its V3521A Integrator Decoupler which will decouple H—H and F—F. (Footnote added in proof.)

number *I* of 1, and the proton (NH) of pyrrole would be expected to show a triplet. Actually, what appears is an extremely broad peak. This comes about because the nitrogen nucleus possesses an electrical quadrupole moment which induces an efficient spin-relaxation. This results in a shortened lifetime for the spin states of the nitrogen nucleus. The proton sees a "moving-picture," and responds with a broad peak. Double irradiation speeds up the process so that the proton sees, essentially, one equivalent state and responds with a sharpened peak. Amide protons behave like the proton on the nitrogen of pyrrole.

The widely published spectrum of ethyl alcohol shows the hydroxylic proton as a single peak. We may well ask why it is not split into a triplet by the methylene protons, and why the methylene quartet is not split further by the hydroxylic proton. The answer is that in a very pure sample of ethanol, this is precisely what is seen. Ordinarily, enough acidic or basic catalyst is present so that intermolecular exchange of the hydroxylic proton is very rapid. The methylene protons see only one equivalent state of the rapidly exchanging hydroxylic protons. Free amines also give a single sharp line because of rapid exchange of the proton attached to nitrogen.

It is interesting to note in one of the exercises in Chapter 6, that a proton on sulfur (mercaptan) is coupled, whereas a hydroxylic proton in the same molecule is not.

We should now be proficient enough to use NMR as an effective tool for assistance in compound identification. We should remember that several other nuclei can be examined at appropriate combinations of magnetic field and frequency. The same general principles elucidated for the proton apply to other nuclei, bearing in mind just four factors: the natural abundance, spin number, nuclear magnetic moment, and the quadrupole moment. These properties of several nuclei of interest to the organic chemist are presented in Appendix E. The effect of the quadrupole moment of the nitrogen nucleus was noted to be a partial decoupling. The more effective quadrupole moment of the chlorine nucleus accounts for its lack of coupling despite its spin number of 3/2; methyl chloride, for example, gives a single peak.

The organic chemist, in viewing a proton spectrum, is most likely to run into coupling (aside from proton coupling) caused by nitrogen, fluorine, carbon-13, and phosphorus. In fact, the presence of one of these elements may be deduced from an otherwise unexplained coupling effect.

Appendix A Charts of Chemical Shifts

There are two thought processes involved in examining an NMR spectrum with the object of identifying an organic compound. These are exemplified by the following questions:

1. What can we expect to find in the vicinity of δ 3.0, τ 7.0?
2. Where would we expect to find the peak of a proton on a carbon atom to which a chlorine atom is attached?

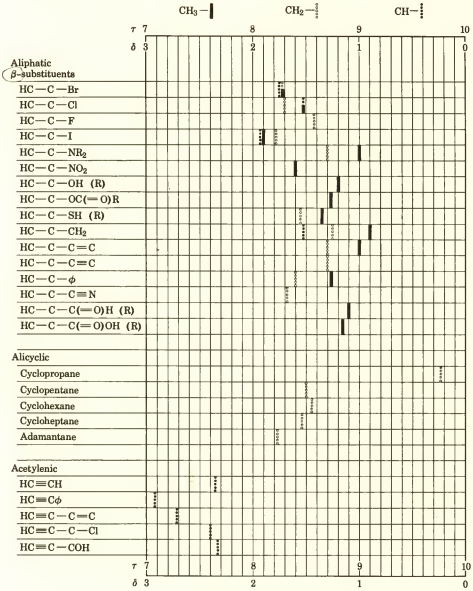
There is as yet no complete source of such information. The NMR Summary prepared by G. V. D. Tiers, Central Research Department, Minnesota Mining and Manufacturing Company, St Paul 6, Minnesota, is a compilation of about 700 proton shifts in τ values, and peak multiplicities. It is a listing of specific compounds in order of increasing τ values. A quick scan affords a partial answer to our first question. A recent publication[15] by Varian Associates, Palo Alto, California, consists of a catalogue of 368 NMR spectra. Over 1400 chemical shifts are listed according to an alphabetical coding system which shows the type of proton, nearest neighboring functional group, and next nearest neighbors. The shifts are cross indexed in order of increased separation from tetramethylsilane (increasing δ). Other useful tables are included in the main references[1–7]. Conroy[4] and Jackman[2], in particular, present useful breakdowns by chemical structure. We have presented a number of chemical shifts in the following chart. Values (δ and τ) assigned are rough averages designed to indicate a region rather than a number. The exact value will vary with solvent and concentration, but, in general, these variations are small in the absence of hydrogen bonding. We have borrowed liberally from all available sources, including unpublished results from these and other laboratories. The chart is a representative survey of groups and structures affecting proton shifts. In many ways, it resembles the Colthup charts used in infrared spectrometry. A separate value is given for methyl, methylene, and methine protons.

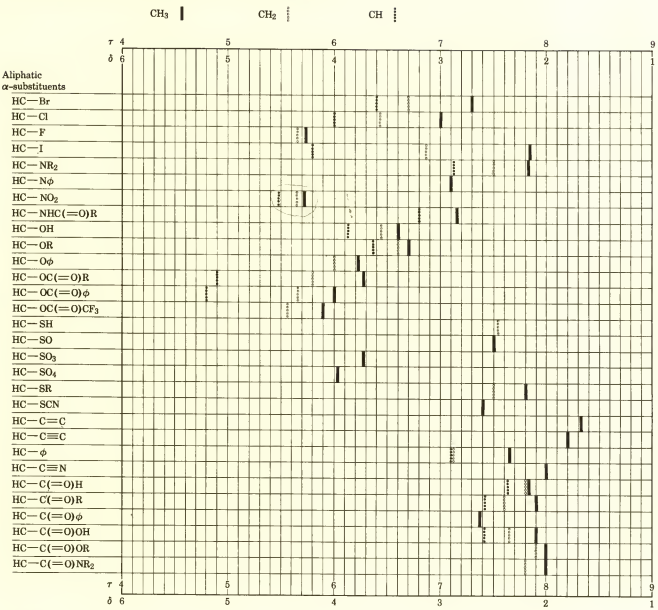
The first line of the second chart, for example, shows that the protons of CH_3Br absorb at about δ 2.7, τ 7.3; the α-protons of RCH_2Br at δ 3.3, τ 6.7; and the α-proton of R_2CHBr at δ 3.6, τ 6.4. Casual inspection of the chart creates the very useful general impression that chemical shifts roughly fall into seven different regions as follows:

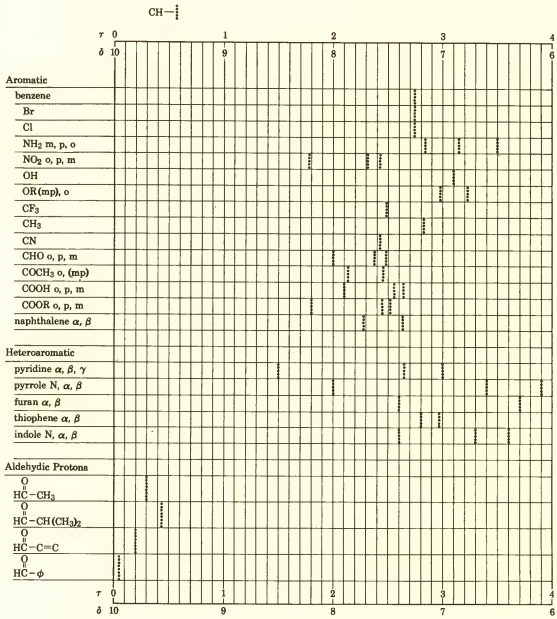
	τ	δ
Aliphatic and alicyclic	8–10	2–0
Aliphatic, β-substituted	8–9.1	2–0.9
Acetylenic	7–8	3–2
Aliphatic, α-substituted (except Si)	5–8.4	5–1.6
Olefinic	2.4–5.5	7.6–4.5
Aromatic and heteroaromatic	1–4	9–6
Aldehydic	0–1	10–9

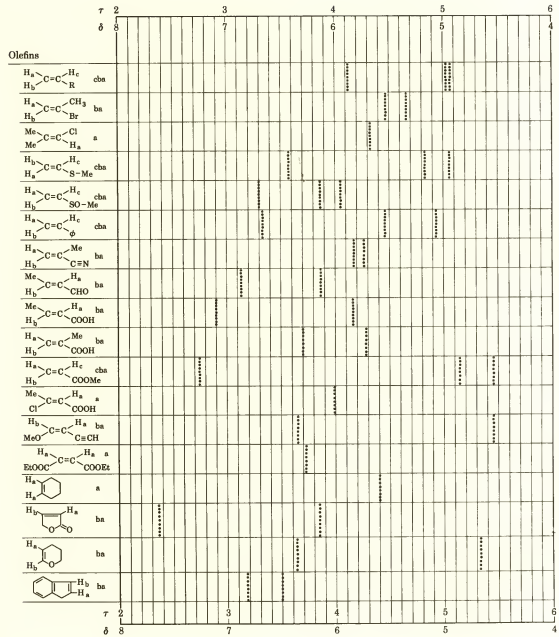
The methyl protons of a hydrocarbon are found at about δ 0.9, τ 9.1. The methylene protons of a hydrocarbon are found at about δ 1.25, τ 8.75. The methine protons of a hydrocarbon are found at about δ 1.5, τ 8.5.

Appendix A Proton Chemical Shifts




CH3
CH2
CH
τ 4 5 6 7 8 9
δ 6 5 4 3 2 1
Aliphatic α-substituents
HC—Br
HC—Cl
HC—F
HC—I
HC—NR2
HC—Nϕ
HC—NO2
HC—NHC(=O)R
HC—OH
HC—OR
HC—Oϕ
HC—OC(=O)R
HC—OC(=O)ϕ
HC—OC(=O)CF3
HC—SH
HC—SO
HC—SO3
HC—SO4
HC—SR
HC—SCN
HC—C=C
HC—C≡C
HC—ϕ
HC—C≡N
HC—C(=O)H
HC—C(=O)R
HC—C(=O)ϕ
HC—C(=O)OH
HC—C(=O)OR
HC—C(=O)NR2


CH—
τ 0 1 2 3 4
δ 10 9 8 7 6
Aromatic
benzene
Br
Cl
NH2 m, p, o
NO2 o, p, m
OH
OR (mp), o
CF3
CH3
CN
CHO o, p, m
COCH3 o, (mp)
COOH o, p, m
COOR o, p, m
naphthalene α, β
Heteroaromatic
pyridine α, β, γ
pyrrole N, α, β
furan α, β
thiophene α, β
indole N, α, β
Aldehydic Protons
O
HC−CH3
O
HC−CH(CH3)2
O
HC−C=C
O
HC−φ
τ 0 1 2 3 4
δ 10 9 8 7 6


τ 2 3 4 5 6
δ 8 7 6 5 4
Olefins
cbn
bn
a
cba
ba
bn
cba
cba
ba
ba
ba
cba
a
bn
a
ba
ba
ba
τ 2 3 4 5 6
δ 8 7 6 5 4

Appendix B Shielding Constants[16] for Disubstituted Methylenes

To obtain a τ value for a disubstituted methylene group, the sum of the appropriate shielding constants for X and Y is subtracted from 9.77 which is the τ value for methane. Thus the value for the methylene protons of ϕ-CH_2—Br is found as follows:

ϕ = 1.85	9.77
Br = 2.33	−4.18
4.18	5.59 = calc. τ value for —CH_2—.

Delta values are obtained by adding the sum of the shielding constants to 0.23. Thus the δ value in this example is

	0.23
	+4.18
	4.41

X or Y	SHIELDING CONSTANTS
—Br	2.33
—Cl	2.53
—I	1.82
—NR_2	1.57
—OH	2.56
—OR	2.36
—Oϕ	3.23
—OCR (O ‖)	3.13
—SR	1.64
—CH_3	0.47
—C=C	1.32
—C≡C	1.44
—ϕ	1.85
—CF_3	1.14
—C≡N	1.70
—RC=O	1.70
—C(OR)=O	1.55
—C(NR_2)=O	1.59

The shielding constants have been used to prepare the chart at bottom of page 88. Several values have been added to the original set of constants.[16]

Appendix C Protons Subject to Hydrogen-Bonding Effects

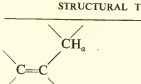
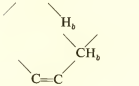
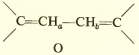
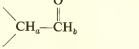
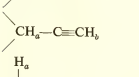
Most of the following chemical shift range data were modified from Reference 3. Values given in the reference in parts per million with respect to external water have been converted to τ values by adding 5.21 parts per million.[17] All values must be taken as very approximate. The lower limit represents neat liquids, the upper limit, dilute solutions or extrapolations to infinite dilution.

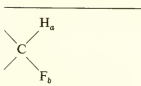
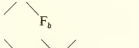
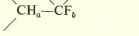
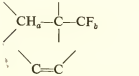
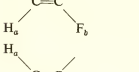
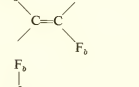
PROTON	CLASS	CHEMICAL SHIFT RANGE τ	δ
OH	Carboxylic acids	−2.0 to −0.4	12.0 to 10.4
	Sulfonic acids	−1.8 to −1.1	11.8 to 11.1
	Phenols	2.9 to 5.8	7.1 to 4.2
	Phenols (intramolecular H-bond)	−2.0 to 4.4	12.0 to 5.6
	Alcohols	4.5 to 9.3	5.5 to 0.7
	Enols (β-diketones, β-ketoesters)	−6.6 to —	16.6 to —
NH_2 and NHR	Alkylamines	5.0 to 9.4	5.0 to 0.6
	Arylamines	5.3 to 7.1	4.7 to 2.9
	Amides	2.0 to 5.0	8.0 to 5.0
SH	Aliphatic mercaptans	8.4 to 8.8	1.6 to 1.2
	Thiophenols	6.4 to 7.2	3.6 to 2.8

Appendix D Proton Spin-Spin Coupling Constants

Most of the following J values in cycles per second are taken with permission from Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in *Organic Chemistry*, Pergamon Press, Oxford.

STRUCTURAL TYPE	J_{ab} CYCLES PER SECOND
CH_a—CH_b	2–9
CH_3—CH_2—R (CH_3: a, CH_2: b)	6.7–7.2
CH_3 / CH_b—R / CH_3 (CH_3: a)	5.7–6.8
H_a / C / H_b	0–20
H_a / C=C / H_b	0–3.5
H_a / C=C / H_b	11–18
H_a H_b / C=C	6–14

STRUCTURAL TYPE	J_{ab} CYCLES PER SECOND
	4–10
	0.5–2.0
	10–13
	1–3
	2–3
	*o* 7–10 *m* 2–3 *p* 1

STRUCTURAL TYPE	J_{ab} CYCLES PER SECOND
	44–81
	7–13
	0
	1–8
	12–40
	*o* 6–10 *m* 5–6 *p* 2

τ Values for Disubstituted Methylenes X—CH_2—Y

SUBSTITUENTS	—Br	—Cl	—ϕ	—NR_2	—OH	—OR	—Oϕ	—OCR (O)	—SR	—CH_3	—C=C—	—C≡C—	—ϕ	—CF_3	—C≡N	—C(R)=O	—C(OR)=O	—C(=O)NR_2
—Br	5.06 5.11	4.84 4.91	5.62	5.87	4.88	5.08	4.21	4.31	5.80	6.57 6.00	6.07 6.12	6.00	5.59	6.30	5.74	5.74	5.89	5.85
—Cl		4.67 4.71	5.01 5.42	5.63	4.68	4.88	4.01	4.11	5.60	6.43 6.77	5.92	5.80	5.39	6.10	5.93 5.54	5.54	5.95 5.69	5.83 5.65
—ϕ			6.13	6.38	5.39	5.59	4.84	4.94	6.31	6.80 7.48	6.13 6.63	6.51	6.10	6.81	6.35 6.25	6.25	6.40	6.36
—NR_2				6.63	5.65	5.85	4.97	5.07	6.56	7.37 7.73	6.70 6.90	6.84	6.52 6.35	7.06	6.50	6.50	6.65	6.60
—OH					4.65	4.85	3.98	4.08	5.57	6.30 6.74	5.87 …	5.72 …	5.42 …	6.07 …	5.51	5.51	5.66	5.62
—OR						5.05	4.18	4.28	5.77	6.60 6.94	6.09	5.97	5.56	6.27	5.80 5.71	5.71	5.78	5.74
—Oϕ							3.31	3.41	4.90	6.07 …	5.22	5.10	4.69	5.40	4.84	4.84	4.91	4.87
—OCR (O)								3.54	5.00	5.75 6.17	5.32 …	5.20	4.79	5.46	4.90	4.90	5.09	5.05
—SR									6.49	7.47 7.66	6.92 6.81	6.69	6.28	6.99	6.43	6.43	6.58	6.54
—CH_3										8.83	7.98	7.86	7.45	8.16	7.60	7.53 7.60	7.75	7.77 7.71
—C=C—											7.13	7.01	6.70 6.66	7.31	6.85 6.75	6.75	6.90	6.86
—C≡C—												6.89	6.48	7.19	6.63	6.63	6.78	6.74
—ϕ													6.03 6.07	6.78	6.35 6.22	6.22	6.37	6.34
—CF_3														7.49	6.93	6.93	7.08	7.04
—C≡N															6.37	6.37	6.52	6.48
—C(R)=O																6.37	6.52	6.48
—C(OR)=O																	6.67	6.63
—C(=O)NR_2																		6.59

Note: The upper number in each case is an experimental value; the lower number is calculated from the shielding constants. Only τ values are given.

ISOTOPE	NMR FREQUENCY mc. FOR A 10 KILOGAUSS FIELD	NATURAL ABUNDANCE (%)	RELATIVE SENSITIVITY AT CONSTANT FREQUENCY	MAGNETIC MOMENT (μ)	SPIN NUMBER	ELECTRICAL QUADRUPOLE MOMENT ($e \times 10^{-24}$ cm^2)
H^1	42.577	99.98	1.000	2.79270	1/2	...
H^2	6.536	1.56×10^{-2}	0.409	0.85738	1	2.77×10^{-3}
B^{11}	13.660	81.17	1.60	2.6880	3/2	3.55×10^{-2}
C^{12}	...	98.9	...	...	0	...
C^{13}	10.705	1.1	0.251	0.70216	1/2	...
N^{14}	3.076	99.62	0.193	0.40357	1	2×10^{-2}
O^{16}	...	99.76	...	...	0	...
F^{19}	40.055	100	0.941	2.6273	1/2	...
Si^{28}	...	92.28	...	...	0	...
P^{31}	17.235	100	0.405	1.1305	1/2	...
S^{32}	...	95.06	...	...	0	...
S^{34}	...	4.2	...	...	0	...
Cl^{35}	4.172	75.4	0.490	0.82089	3/2	-7.97×10^{-2}
Cl^{37}	3.472	24.6	0.408	0.68329	3/2	-6.21×10^{-2}
Br^{79}	10.667	50.57	1.26	2.0990	3/2	0.33
Br^{81}	11.498	49.43	1.35	2.2626	3/2	0.28
I^{127}	8.519	100	2.33	2.7939	5/2	−0.75

Appendix E Properties of Several Nuclei

The following nuclei are encountered by the organic chemist. Their magnetic properties were taken with permission from Varian Associates NMR Table, 3rd ed., revised August 1955.

References

1. Jackman, L. M., *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, New York, 1959.
2. Roberts, J. D., *Nuclear Magnetic Resonance Applications to Organic Chemistry*, McGraw-Hill, New York, 1959.
3. Pople, J. A., W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959.
4. Conroy, H., "Nuclear Magnetic Resonance in Organic Structural Elucidation," in *Advances in Organic Chemistry*, R. A. Raphael, E. C. Taylor, and Hans Wynberg, eds., Vol. II, Interscience, New York, 1960.
5. Gutowsky, H. S., "Nuclear Magnetic Resonance," in *Technique of Organic Chemistry*, Vol. I, Part IV, 3rd ed., Interscience, New York, 1960.
6. Foster, H., "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Analysis," in *Organic Analysis*, Vol. IV, Interscience, New York, 1960.
7. Andrews, E. R., *Nuclear Magnetic Resonance*, Cambridge University Press, New York, 1955.
8. Varian Associates, unpublished results.
9. Goodman, L., R. M. Silverstein, and A. Benitez, *J. Am. Chem. Soc.*, **79**, 3073 (1957).
10. Roberts, J. D., *Nuclear Magnetic Resonance Applications to Organic Chemistry*, McGraw-Hill, New York, 1959, p. 49.
11. Karplus, M., *J. Chem. Phys.*, **30**, 11 (1959). M. Karplus and D. H. Anderson, *Ibid.* **30**, 6 (1959).
12. Conroy, H., "Nuclear Magnetic Resonance in Organic Structural Elucidation," in *Advances in Organic Chemistry*, Vol. II, Interscience, New York, 1960, p. 311.
13. Roberts, J. D., "An Introduction to the Analysis of Spin-Spin Splitting," in *High Resolution NMR Spectra*, W. A. Benjamin, New York, 1961.
14. Manatt, S. L. and D. D. Elleman, *J. Am. Chem. Soc.*, **83**, 4095 (1961). R. Freeman, *J. Molec. Phys.*, **3**, 435 (1960).
15. Varian Associates, *High Resolution NMR Spectra Catalogue*, 1962.
16. Shoolery, J. N., *Technical Information Bulletin*, **2**, No. 3, Varian Associates, Palo Alto, Calif. B. P. Dailey, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).
17. Tiers, G. V. D., *J. Phys. Chem.*, **62**, 1151 (1958).

CHAPTER FIVE

Ultraviolet Spectrometry

INTRODUCTION

Absorption spectrometry, using ultraviolet and visible light, was one of the earliest physical methods employed in the examination of molecular structure.

Molecular absorption in the ultraviolet region is of interest to the organic chemist because absorption is dependent upon the electronic structure of the molecule. An ultraviolet or electronic spectrum is the energy absorption pattern obtained when a substance is subjected to radiation in the ultraviolet region of the electromagnetic spectrum. The ultraviolet spectrum is a plot of the wavelength or frequency of absorption versus the absorption intensity (transmittance or absorbance). Spectral data are often presented in other forms in which the absorption intensity is expressed as molar absorptivity, ϵ or $\log \epsilon$ (vide infra). One presentation consists of a graphical plot of wavelength versus ϵ or $\log \epsilon$. The data may also be presented in tabular form. The table indicates wavelengths at which maximum absorption occurs (λ_{max}), and the molar absorptivities (ϵ_{max}) or logarithms of molar absorptivities ($\log \epsilon_{max}$) at the wavelengths of maximum absorption. Ultraviolet absorption data are presented in tabular form in Chapters 6 through 8.

A detailed mathematical treatment of the origin of

ultraviolet or electronic spectra is beyond the scope of this chapter. However, enough of the theory will be described to acquaint the organic chemist with the origin of the spectra and with spectral interpretation.

Ultraviolet spectra reveal fewer structural features than infrared spectra. All organic compounds show characteristic absorption in the infrared, whereas many compounds are transparent in the near ultraviolet. Nevertheless, many compounds, with specific electronic structures—for example, ketones, aldehydes, and aromatic compounds—show characteristic ultraviolet absorption. This absorption can be very valuable in the elucidation of molecular structure.

The data obtained from ultraviolet spectra will be used in conjunction with other spectral data in our determination of molecular structure. In many cases, the ultraviolet data will serve to confirm structural characteristics indicated by other spectral data.

Ultraviolet spectrophotometers are commonplace in the modern chemical laboratory. The organic chemist will frequently have an ultraviolet spectrophotometer available for personal use. A number of manually operated and automatic recording spectrophotometers are available in the price range of $2000 to $17,000.

An abundance of reference material, relating to the theory and interpretation of ultraviolet spectra, is available. One of the most useful references for the organic chemist is the text of Gillam and Stern.[1] The excellent discussions by Braude[2,3] will prove useful for obtaining a background in the interpretation of ultraviolet spectra. The theory of electronic spectra has been extensively reviewed by Duncan and Matsen,[4] Bauman,[5] and Jaffé and Orchin.[6] Several excellent compilations of ultraviolet spectra and absorption data are available.[7–13] Volumes III, IV, and V of the series *Electronic Spectral Data*,[7,8] are now in preparation. These additional volumes will include ultraviolet spectral data published through 1961.

THEORY

Wavelengths in the ultraviolet region are expressed in millimicrons, mμ (1 mμ = 10^{-7} cm) or Angstroms, Å (1 Å = 10^{-8} cm). The ultraviolet portion of the electromagnetic spectrum extends over the region of 10–380 mμ or 100–3800 Å. The near ultraviolet or quartz ultraviolet region, accessible via the quartz spectrophotometer, extends between 200 and 380 mμ. The far ultraviolet portion of the spectrum covers the region below 200 mμ.

The total energy of a molecule is the sum of its electronic or binding energy and its kinetic energy. The absorption of infrared radiation, which produces changes in the kinetic energy of the molecule, has already been described in Chapter 3.

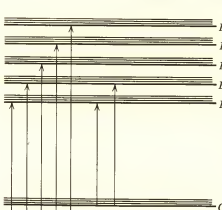


Fig. 1. Energy-level diagram of a diatomic molecule.

The electronic or binding energy is the largest component of the total energy of a molecule. Energy absorbed in the ultraviolet region produces electronic transitions within the molecule. The relationship between the energy absorbed, in an electronic transition, and the frequency (ν) or wavelength (λ) of radiation producing the transition, is expressed by the following equation:

$$\Delta E = h\nu = hc/\lambda$$

where h is Planck's constant and c is the velocity of light. ΔE is the energy absorbed in bringing about an electronic transition in a molecule from its lowest energy state (ground state) to an excited state. The energy absorbed is quantized. The smaller the energy difference between the ground state and the excited state, the longer will be the wavelength of absorption.

The absorption spectrum, arising from an electronic transition, would consist of a single discrete line if each electronic state were not accompanied by vibrational and rotational sublevels.

The spectra of simple molecules, in the gaseous state, consist of narrow absorption peaks, each representing a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. This is shown schematically in Figure 1 in which the vibrational levels are designated v_0, v_1, v_2, and so forth.

At ordinary temperatures most of the molecules in the electronic ground state will be in the zero vibration level (Gv_0); consequently, the most probable electronic transitions are from that level.

In more complex molecules containing more atoms, the multiplicity of vibrational sublevels and the closeness of their spacing cause the discrete bands to coalesce, and broad absorption bands or "band envelopes" are obtained.

The principal characteristics of an absorption band are its position and intensity. The position of maximum absorption (λ_{max}) corresponds to the wavelength of

radiation whose energy is equal to that required for an electronic transition.

The intensity of absorption is largely dependent upon two factors: the probability of occurrence of interaction between the radiation energy and the electronic system to raise the ground level to an excited state; and the polarity of the excited state. Intense absorption occurs when the excited state involves large electrical moments. Absorption with $\epsilon_{max} > 10^4$ is high intensity absorption; low intensity absorption corresponds to ϵ_{max} values $< 10^3$. Transitions of low probability are forbidden transitions. The intensity of absorption may be expressed as transmittance. Transmittance is defined by the following equation:

$$\text{Transmittance } (T) = I/I_0$$

where I_0 is the intensity of the radiant energy striking the sample and I is the intensity of the radiation emerging from the sample. A more convenient expression of absorption intensity is that derived from the Lambert-Beer law which establishes a relationship between the transmittance, the sample thickness, and the concentration of the absorbing species. This relationship is expressed as follows:

$$\log_{10} I_0/I = kcb = A$$

where k = a constant characteristic of the solute
c = concentration of solute
b = path length through the sample
A = absorbance or optical density

When c is expressed in moles per liter, and the path length (b) through the sample is expressed in centimeters, the preceding expression becomes

$$A = \epsilon cb$$

The term ϵ is now known as the molar absorptivity; it was formerly called the molar extinction coefficient.[14]

The intensity of an absorption band in the ultraviolet spectrum is usually expressed as the molar absorptivity at maximum absorption, ϵ_{max} or $\log \epsilon_{max}$.

When the constitution of an absorbing material is unknown, the absorptivity may be expressed as

$$E^{1\%}_{1\,cm} = A/cb$$

where
c = concentration in grams per 100 ml
b = path length through the sample in centimeters

Before continuing further with a discussion of the ultraviolet spectra, it will be advantageous to define several terms which are frequently used in the discussion of electronic spectra.

CHROMOPHORE. A covalently unsaturated group responsible for electronic absorption.

AUXOCHROME. A saturated group which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption maximum.

BATHOCHROMIC SHIFT. The shift of absorption to a longer wavelength due to substitution or solvent effect.

HYPSOCHROMIC SHIFT. The shift of absorption to a shorter wavelength due to substitution or solvent effect.

HYPERCHROMIC EFFECT. An increase in absorption intensity.

HYPOCHROMIC EFFECT. A decrease in absorption intensity.

Types of Electrons

Electronic transitions in organic molecules can be classified on the basis of the types of electrons involved in the transitions. The characteristic absorption arising from these transitions will serve as a basis for the discussion of ultraviolet spectra.

Sigma (σ) Electrons

The single valence bonds of saturated hydrocarbons contain σ-electrons only. The σ-electrons are tightly bound; the energy required to disrupt or remove them is available only in the far ultraviolet region. Since transitions involving the σ-electrons are not observed in the near ultraviolet, no further mention will be made of them.

n-Electrons

The n-electrons are the nonbonding electrons of hetero atoms such as nitrogen, oxygen, halogen, or sulfur. n-Electrons are less firmly bound than σ-electrons. n-Electrons undergo two types of transitions: an $n \rightarrow \pi^*$ transition, such as occurs in the carbonyl group (vide infra) and an $n \rightarrow \sigma^*$ transition, such as occurs in ethers, alcohols, amines, sulfides, disulfides, and alkyl halides. Alcohols and ethers absorb strongly in the far ultraviolet region at longer wavelengths than the saturated hydrocarbons but are transparent in the near ultraviolet region. Sulfides, disulfides, alkyl iodides, and amines absorb in the near ultraviolet region as a consequence of the more weakly held n-electrons.

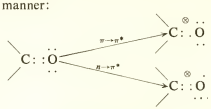
The auxochromic effect of atoms containing n-electrons will be discussed later.

π-Electrons

The unsaturated bonds of chromophores consist of π-electrons in addition to a pair of σ-electrons. The π-electrons are less tightly bound than the σ-electrons and undergo transitions at longer wavelengths. Compounds containing single ethylenic, acetylenic, nitrile, sulfone, azomethine, and amido groups absorb in the far ultraviolet but show no absorption in the near ultraviolet. Compounds which contain single carbonyl, carboxyl, azo, nitro, nitroso, nitrate, nitrite, or sulfoxide groups show absorption at wavelengths longer than 200 mμ.

The strong absorption in the far ultraviolet region results from a $\pi \rightarrow \pi^*$ transition, that is, the transition of a π-electron to a higher energy orbital (antibonding orbital).

The weak absorption in the near ultraviolet region involves an $n \rightarrow \pi^*$ transition. These transitions, occurring in a carbonyl group, can be represented simply in the following manner:

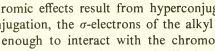


(⊗ = excited electron)

Electronic interaction can produce marked changes in the character of electronic spectra. Such interaction occurs in two types of structures: π–π structures, in which two groups containing π-electrons are adjacent; and n–π structures, in which an atom, containing n-electrons (nonbonding), is adjacent to a group containing π-electrons. The π-electrons are delocalized throughout the conjugated system. In π–π conjugated systems, such as butadiene (C═C—C═C), the absorption is shifted to the higher-wavelength region of the spectrum (bathochromic shift). The absorption is very intense.

Groups, such as the hydroxyl or amino group, are known as auxochromic groups or auxochromes. The hetero atom in the auxochromes possesses nonbonding or n-electrons. Many isolated auxochromic groups, like many of the single chromophoric groups, show intense absorption in the far ultraviolet but no absorption in the near ultraviolet. Attachment of an auxochrome to an unsaturated group (chromophore) results in n–π conjugation, with an accompanying bathochromic shift to the near ultraviolet and an increase in absorption intensity. The majority of compounds which show appreciable absorption at wavelengths >200 mμ are conjugated, either π–π or n–π.

Slight auxochromic effects are also produced by the attachment of alkyl radicals to chromophoric groups. The auxochromic effects result from hyperconjugation. In hyperconjugation, the σ-electrons of the alkyl group are mobile enough to interact with the chromophoric group to produce a change of charge distribution within the molecule. This interaction may be represented schematically in the following manner:



Charge-Electrons and Unpaired Electrons

Ultraviolet absorption results from the excitation of two other types of electrons; charge-electrons and unpaired electrons. The absorption spectrum of the triphenylmethyl ion is an example of a "charge-resonance" spectrum resulting from the migration of a permanent charge-electron. Transitions in the triphenylmethyl radical are responsible for low-intensity absorption in the ultraviolet known as "electron-resonance" absorption. These will be of no further concern to us.

Types of Absorption Bands *

Four types of absorption bands are recognized in the spectra of organic molecules; *R*-bands, *K*-bands, *E*-bands and *B*-bands. A single spectrum seldom shows all four band types. Recognition of these bands, in the spectra of organic molecules, and an understanding of their origin and relation to structure are necessary for the interpretation of ultraviolet spectra.

R-Bands (German radikalartig) have their origin in the $n \rightarrow \pi^*$ transitions of single chromophoric groups such as the carbonyl or nitro group. The *R*-bands are characterized by low molar absorptivities; $\epsilon_{max} < 100$. They frequently remain in the spectra when modifications in molecular structure introduce additional bands. When additional bands make their appearance the *R*-bands are shifted to longer wavelengths.

K-Bands (German konjugierte) appear in the spectra of molecules which have π–π conjugated structures such as butadiene or 1,3,5-hexatriene. The *K*-bands result from $\pi \rightarrow \pi^*$ transitions and are characterized by high molar absorptivity, $\epsilon_{max} > 10{,}000$.

K-Bands also appear in the spectra of aromatic compounds possessing chromophoric substitution—acetophenone or styrene. *K*-Bands move to longer wavelengths and become more intense as the number of conjugated units increases. The *K*-bands of conjugated chromophoric substituted aromatics occupy about the same position as the *E*-bands (vide infra) of auxochromic substituted aromatics (200–250 mμ).

Spectra of α,β-diketones do not show a *K*-band, probably because of the reluctance of the oxygen atoms to acquire opposite formal charges, O═C—C═O $\rightarrow$ $^{+}$O—C═C—O^{-}.[2]

B-Bands (Benzenoid bands) are characteristic of the spectra of aromatic or heteroaromatic molecules. Benzene shows a broad absorption band, containing multiple peaks or fine structure, in the near ultraviolet region between 230 and 270 mμ (ϵ of most intense peak ca. 230). The fine structure arises from vibrational sublevels accompanying the electronic transitions. When chromophoric substitution exists in the aromatic ring, the

* We use the classification of bands credited to A. Burawoy. Although Burawoy's description of the electronic origin of these bands is archaic, his correlations remain a useful mnemonic tool for the organic chemist if used in conjunction with a modern description of electronic transitions.

Table I Summary of Electronic Structure and Transitions

ELECTRONIC STRUCTURE	EXAMPLE	TRANSITION	$\lambda_{max}(m\mu)$	ϵ_{max}	BAND
σ	Ethane	$\sigma \rightarrow \sigma^*$	135	...	...
n	Water	$n \rightarrow \sigma^*$	167	7,000	...
	Methanol	$n \rightarrow \sigma^*$	183	500	...
	1-Hexanethiol	$n \rightarrow \sigma^*$	224	126	...
	n-Butyliodide	$n \rightarrow \sigma^*$	257	486	...
π	Ethylene	$\pi \rightarrow \pi^*$	165	10,000	...
	Acetylene	$\pi \rightarrow \pi^*$	173	6,000	...
π and n	Acetone	$\pi \rightarrow \pi^*$	188	900	...
	Acetone	$n \rightarrow \pi^*$	279	15	*R*
π-π	1,3-Butadiene	$\pi_1 \rightarrow \pi^*$	220	30,000	*K*
	1,3,5-Hexatriene	$\pi_1 \rightarrow \pi^*$	258	35,000	*K*
π-π and n	Acrolein	$\pi \rightarrow \pi^*$	210	25,500	*K*
		$n \rightarrow \pi^*$	315	13.8	*R*
Aromatic π	Benzene	Aromatic $\pi \rightarrow \pi^*$	ca 200	8,000	*E*
		Aromatic $\pi \rightarrow \pi^*$	255	215	*B*
Aromatic π-π	Styrene	Aromatic $\pi \rightarrow \pi^*$	244	12,000	*K*
		Aromatic $\pi \rightarrow \pi^*$	282	450	*B*
Aromatic π-σ (Hyperconjugated)	Toluene	Aromatic $\pi \rightarrow \pi^*$	208	2,460	*E*
		Aromatic $\pi \rightarrow \pi^*$	262	174	*B*
Aromatic π-π and n	Acetophenone	Aromatic $\pi \rightarrow \pi^*$	240	13,000	*K*
		Aromatic $\pi \rightarrow \pi^*$	278	1,110	*B*
		$n \rightarrow \pi^*$	319	50	*R*
Aromatic π-n (Auxochromic)	Phenol	Aromatic $\pi \rightarrow \pi^*$	210	6,200	*E*
		Aromatic $\pi \rightarrow \pi^*$	270	1,450	*B*

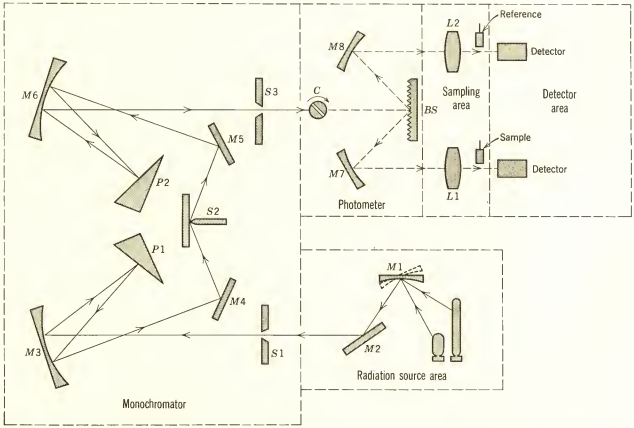


Fig. 2. Optical layout of a Double-Beam Ultraviolet Spectrophotometer. (Courtesy of Perkin-Elmer Corporation, Norwalk, Conn.)

B-bands are observed at longer wavelengths than the more intense *K*-bands; for example, styrene, *K*-band λ_{max} 244 mμ (ϵ_{max} 12,000), *B*-band λ_{max} 282 mμ (ϵ_{max} 450). When an *R*-band appears in the spectrum of an aromatic compound which contains *K*- and *B*-bands, the *R*-band is shifted to longer wavelengths beyond the *B*-band. The spectrum of benzaldehyde shows *K*-, *B*-, and *R*-bands. The characteristic fine structure of the *B*-bands may be lost in some of the aromatic derivatives. The fine structure is often destroyed by the use of polar solvents.

E-Bands (Ethylenic bands) like the *B*-bands are characteristic of the spectra of aromatic structures. The origin of the *E*-band is ascribed to electronic transitions in the benzenoid system of three ethylenic bonds in closed cyclic conjugation.[3] The *E*-band of benzene is not observed in the near ultraviolet region. Auxochromic substitution, however, brings the *E*-band into the near ultraviolet region, although in many cases it may not appear at wavelengths much over 210 mμ. The molar absorptivity is variable but generally ranges between 2000 and 14,000. The bathochromic shift is related to the ease with which the unshared electrons of the hetero atoms can participate in the resonance of the aromatic system. With the appearance of the *E*-band as a result of auxochromic substitution, the *B*-band shifts to longer wavelengths and frequently increases in intensity. Molecules such as benzylidene acetone, in which more complex conjugated chromophoric substitution occurs, produce spectra with both *E*- and *K*-bands; the *B*-bands are obscured by the displaced *K*-bands.

The electronic structures responsible for absorption and the electronic transitions involved are briefly summarized in Table 1.

INSTRUMENTATION

A modern, recording photoelectric spectrophotometer, consists of five sections or areas: (1) radiation source, (2) monochromator, (3) photometer, (4) sample area, and (5) detector area. The optical layout of a typical double-beam instrument is presented in Figure 2.

Radiation Source

The radiation source for the ultraviolet region of the spectrum is a hydrogen discharge tube. The hydrogen discharge tube can be replaced by a tungsten incandescent lamp when absorption in the visible region is to be determined. Mirror *M*1 is rotated manually to focus the light emitted from either source onto the entrance slit (*S*1) of the monochromator.

Monochromator

The light from the source is dispersed into its separate wavelengths by the monochromator. The light which enters through entrance slit *S*1 is collimated into parallel rays by the spherical mirror *M*3 and is reflected to quartz prism *P*1. After the light has passed through prism *P*1, it is reflected back through the prism by a mirrored surface on the back of the prism. Dispersion takes place during both passes through the prism. The light which emerges from *P*1 is reflected to the intermediate slit *S*2 by mirrors *M*3 and *M*4. Since a dispersing prism inherently produces a curved image of a straight slit, entrance slit *S*1 is curved to compensate for the curvature produced in the first stage of the monochromator. The image which strikes the intermediate slit *S*2 is essentially straight. Slit *S*2 consists of a single fixed jaw normal to a mirror. The second jaw of the slit is the image of the fixed jaw in the mirror. The mirror, at slit *S*2, reverses the field of the beam so that comatic aberration introduced by the first stage of the monochromator is removed by the second stage of the monochromator. The light path through the second stage (M5, M6, and P2) is the mirror image of that through the first stage.

The two prisms *P*1 and *P*2 are rotated simultaneously. The wavelength of radiation which appears at exit slit *S*3 is determined by the angular position of the prisms. The rotating mechanism for the prisms is coupled to the recording drum. The double monochromator has two advantages: It doubles dispersion and reduces stray light. Stray light consists of the unwanted wavelengths appearing at slit *S*3. Slit *S*3 is curved to compensate for curvature reintroduced by the second stage of the monochronometer.

Photometer

The monochromatic light which emerges from exit slit *S*3 is pulsed by chopper *C* and split into sample and reference beams by the beam splitter *BS*. The reference and sample beams, reflected from the beam splitter, are reflected by mirrors *M*7 and *M*8, through lenses *L*1 and *L*2 to the sample area. Lenses *L*1 and *L*2 serve to optimize the parallel nature of the rays which pass through the sample area. Optics for the transmission of ultraviolet radiation are made of quartz.

Sample Area

The beams entering the sample area become more concentrated as they pass through the area toward the detectors; that is, the cross sections of the beams become smaller. Small cells are usually placed in the region nearest the detector area. A great variety of cells is

available depending upon the specific needs of the investigator.

The photomultiplier tubes of the detector area are protected from exposure to excessively bright light by automatic shutters which seal the detector area when the sample area is opened.

Detector Area

The radiation beams which pass into the detector area are focused on separate photomultiplier tubes. The radiation which falls on the photomultiplier tubes creates a voltage proportional to the energy which strikes the detectors. The off-balance voltage, resulting from absorption of energy from the sample beam, is balanced by an equivalent voltage tapped from a portion of a slidewire. The recorder pen travels with the contacts on the slidewire. When a linear slidewire is used, the spectra are recorded as wavelength versus transmittance. Since the absorbance (A) equals $\log 1/T$, the use of a slidewire, whose resistance varies logarithmically with length, results in a recording linear with respect to absorbance.

SAMPLE HANDLING

Ultraviolet spectra of compounds are usually determined either in the vapor phase or in solution.

A variety of quartz cells is available for the determination of spectra in the gaseous phase. These cells are equipped with gas inlets and outlets and have path lengths from 0.1 mm to 100 mm. Cell jackets are available through which liquids may be circulated for temperature control.

Cells used for the determination of spectra in solution vary in path length from 1 cm to 10 cm. One-centimeter square, quartz cells are commonly used. The square cells require about 3 ml of solution. Filler plugs are available to reduce the volume in the 1 cm square cell. Narrower cells with 1 cm path lengths are also available. Microcells, made of a teflon capillary and quartz windows, may also be used when only a small amount of solution is available. The use of a beam condenser, to minimize the loss of energy, is advisable when the microcells are used.

In the preparation of a solution, a sample is accurately weighed and made up to volume in a volumetric flask. Aliquots are then removed and additional dilutions made until the desired concentration has been acquired. Cleanliness of the cells is of utmost importance. The cells should be rinsed several times with solvent and checked for absorption between successive determinations. It may be necessary to clean the cells with a detergent or hot nitric acid to remove traces of previous samples.

Many solvents are available for use in the ultraviolet region. Three common solvents are cyclohexane, 95% ethanol, and 1,4-dioxane.

A spectrographic grade of cyclohexane is available. Cyclohexane may be freed of aromatic impurities by percolation through activated silica gel. It is a very desirable solvent for aromatic compounds, particularly the polynuclear aromatics. Also, the spectra of aromatic compounds generally retain their fine-line structure when determined in cyclohexane. The fine-line structure is often lost in more polar solvents. Cyclohexane is transparent down to 210 mμ.

Ninety-five percent ethanol is generally a good choice when a more polar solvent is required. This solvent can

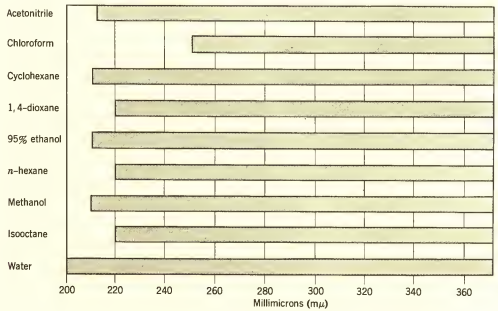


Fig. 3. Useful transparency ranges of solvents in near ultraviolet region.

generally be used as purchased, without further purification, but absolute ethanol must be freed of benzene used in its preparation. The lower limit of transparency of ethanol is near 210 mμ.

Dioxane can be purified by distillation from sodium. Benzene contamination can be removed by the addition of methanol followed by distillation to remove the benzene-methanol azeotrope.[9] 1,4-Dioxane is transparent down to about 220 mμ. Ultraviolet transparency data for a number of solvents are presented in Figure 3.

Care should be exercised to choose a solvent which will be inert to the solute. For example, the spectra of aldehydes should not be determined in alcohols. Photochemical reactions may be detected by checking for changes in absorbance with time after exposure to the ultraviolet beam in the instrument.

CHARACTERISTIC ABSORPTION OF ORGANIC COMPOUNDS

In our discussion of the theory of electronic or ultraviolet spectra, it was shown that the ability of a compound to absorb ultraviolet irradiation is dependent upon its electronic structure. Those structures in which electronic transitions can take place with the absorption of a minimum of energy absorb at relatively long wavelengths, whereas electronic structures which require maximum energy for electronic transitions absorb at shorter wavelengths.

The absorption characteristics of organic molecules depend not only upon the types of electrons which are present, but also upon their ability to interact, that is, enter into conjugation.

The effect of substitution upon the absorption characteristics of specific electronic structures is of interest to the organic chemist.

Compounds Containing Only σ-Electrons

Saturated hydrocarbons contain σ-electrons exclusively. Since the energy required to bring about ionization of the σ-bonds is of the order of 185 kcal per mole and is available only in the far ultraviolet region, saturated hydrocarbons are transparent in the near ultraviolet region.

Saturated Compounds Containing *n*-Electrons

Saturated compounds containing hetero atoms such as oxygen, nitrogen, sulfur, or halogen, possess nonbonding electrons (*n*-electrons) in addition to σ-electrons. Many compounds of this type show no absorption in the near ultraviolet. However, thiols, sulfides, amines disulfides, and iodides absorb in the near ultraviolet. Absorption data for some typical saturated sulfur compounds are presented in Table II.

Table II Absorption Characteristics of Saturated Sulfur Compounds **(λ_{max} mμ)**

COMPOUND	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	SOLVENT
2-Butanethiol	...	...	231(s)*	126	Cyclohexane
1-Hexanethiol	...	...	224(s)	126	Cyclohexane
Di-*n*-butyl sulfide	210	1200	229(s)	145	Alcohol
Di-*i*-butyl sulfide	213	2600	...	...	Alcohol
Di-*n*-butyl disulfide	204	2089	251	398	Alcohol
Dicyclohexyl disulfide	...	...	248	560	Alcohol

* Shoulder or inflection.

Compounds Containing π-Electrons

Single Chromophores (*Isolated Unsaturation*)

Not all of the so-called chromophoric groups lead to absorption in the near ultraviolet, although these groups may absorb strongly in the far ultraviolet; for example, the nitriles and sulfones. Other groups, such as the nitrite group and the sulfoxide group, absorb in the near ultraviolet. The majority of the groups which absorb in the near ultraviolet show weak absorption.

The absorption characteristics of some compounds containing single chromophoric groups are presented in Table III.

ETHYLENIC GROUP. Aliphatic compounds containing a single ethylenic group show no absorption in the near ultraviolet, although all show intense absorption in the far ultraviolet. Compounds which contain multiple isolated ethylenic linkages, such as 1,5-hexadiene, also absorb in the far ultraviolet.

CARBONYL GROUP. One of the most important chromophores is the carbonyl group of ketones and aldehydes. The ketones and aldehydes show intense absorption in the far ultraviolet due to a $\pi \rightarrow \pi^*$ transition. All saturated ketones and aldehydes also show weak absorption (*R*-bands) in the near ultraviolet region resulting from an $n \rightarrow \pi^*$ transition. Ketones absorb in the near ultraviolet at 270–285 mμ ($\epsilon_{max} < 30$). The absorption bands of aldehydes are similar to those of ketones, but they occur at somewhat longer wavelengths, 280–300 mμ. Absorption data for several saturated ketones and aldehydes are presented in Table IV.

Both substitution and solvent have an effect on the absorption maxima of ketones and aldehydes. The bathochromic effect of substitution can be seen by comparing the absorption data, presented in Table IV, for acetone, methyl ethyl ketone, methyl *t*-butyl ketone, and hexamethylacetone. The absorption maxima of ketones

Table III Absorption Data for Isolated Chromophores

CHROMOPHORIC GROUP	SYSTEM	EXAMPLE	λ_{max} (mμ)	ϵ_{max}	SOLVENT
Ethylene	RCH=CHR	Ethylene	193	10,000	Vapor
Acetylene	R—C≡C—R	Acetylene	173	6,000	Vapor
Carbonyl	$RR_1C{=}O$	Acetone	188	900	*n*-Hexane
			279	15	...
Carbonyl	RHC=O	Acetaldehyde	293.4	11.8	Alcohol
Carboxyl	RCOOH	Acetic acid	204	60	Water
Amido	$RCONH_2$	Acetamide	<208	...	...
Azomethine	>C=N—	Acetoxime	190	5,000	Water
Nitrile	—C≡N	Acetonitrile	<160	...	...
Azo	—N=N—	Azomethane	347	4.5	...
Nitroso	—N=O	Nitrosobutane	300	100	Ether
			665	20	
Nitrate	$-ONO_2$	Ethyl nitrate	270	12	Dioxane
Nitro		Nitromethane	271	18.6	Alcohol
Nitrite	—ONO	Amyl nitrite	218.5	1,120	Petroleum ether
			356.5†	56	
Sulfoxide		Cyclohexyl methyl sulfoxide	210	1,500	Alcohol
Sulfone		Dimethyl sulfone	<180	...	...

Reproduced in part by permission from A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold, London, 2nd ed., 1957.
† Most intense peak of fine structure group.

are markedly affected by hydrogen bonding with solvents. For example, λ_{max} of acetone in *n*-hexane occurs at 279 mμ; in water the λ_{max} is 264.5 mμ. The absorption maxima, in solvents of intermediate polarity, are intermediate between these two values. The effect of the solvent on the molar absorptivity is very small.

Table IV Absorption Data for Soturoted Ketones ond Aldehydes

COMPOUND	*R*-BAND		SOLVENT
	λ_{max} (μ)	ϵ_{max}	
Acetone	272.5	18.6	Alcohol
Methyl ethyl ketone	273	18.2	Alcohol
Methyl *t*-butyl ketone	285	21.2	...
Hexamethylacetone	295	20	Alcohol
Acetaldehyde	293.4	11.8	Alcohol
Propionaldehyde	277.5	13.2	Water
Butyraldehyde	290	17.8	Hexane

Since the absorption bands of ketones and aldehydes are weak, spectra of derivatives such as the semicarbazones or 2,4-dinitrophenylhydrazones are often used for identification work.

The absorption characteristics of the carbonyl group, in saturated carboxylic acids and esters, are markedly effected by the adjacent hydroxyl or alkoxyl group. Saturated carboxylic acids and their saturated esters absorb weakly near 200–210 mμ. Acyl halides and anhydrides absorb weakly at higher wavelengths than the parent acids. For example, acetyl chloride absorbs at 234.5 mμ; acetic anhydride at 217 mμ.

MULTIPLE-BONDED NITROGEN GROUPS. Saturated alkyl compounds which contain nitrogen multiply bonded to carbon, (azomethine and nitrile groups) do not absorb in the near ultraviolet.

The azido-, azo-, and diazo groups, consisting of multiply linked nitrogen atoms, all show weak *R*-bands (ϵ_{max} 3–25) in the region of 285–400 mμ. Some azides and diazo compounds also exhibit a short-wavelength band at 200–250 mμ. Diazo compounds show maximum absorption at the long-wavelength end of the 285–400 mμ region.

Four groups contain multiple nitrogen to oxygen linkages: nitro, nitroso, nitrates, and nitrites. Saturated

compounds which contain the nitro, nitrate, or nitrite group all absorb in the near ultraviolet. Primary, secondary, and tertiary aliphatic nitro compounds absorb in the 270–280 mμ region ($\epsilon_{max} < 100$). Nitroso compounds absorb near 300 mμ and also absorb weakly in the visible region near 670 mμ.

Aliphatic nitrates show weak absorption near 270 mμ. The spectra of nitrates are generally characterized by an inflection or shoulder rather than a well defined maxima.

Nitrites are generally characterized by an absorption band in the 220–230 mμ region (ϵ_{max} 1000–2000) and a broad weak absorption band in the 300–400 mμ region. The latter band contains fine structure resembling the *B*-bands of aromatics. This effect presumably results from resonance in the —O—N=O group, since each of the atoms has unshared electrons.

MULTIPLE-BONDED SULFUR GROUPS. Sulfones and sulfoxides contain multiple-bonded sulfur groups. Aliphatic sulfones are transparent in the near ultraviolet. Spectra of aliphatic sulfoxides exhibit a broad band of medium intensity near 210 mμ.

Multiple Chromophores (π–π Conjugation)

Conjugation decreases the energy required to bring about electronic transitions.

CONJUGATED OLEFINS. Acyclic conjugated dienes show an intense *K*-band in the near ultraviolet near 215–230 mμ. The intensities (ϵ) vary between 17,000 and 26,000. Open-chain conjugated trienes absorb at longer wavelengths with higher intensity than the conjugated dienes. Additional units in the conjugated systems extend the absorption into the visible region with absorption intensities up to 200,000.

The attachment of an auxochromic group to the end of a conjugated polyene system, H—(C=C)$_n$OH, causes a marked bathochromic shift of the *K*-band.

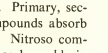
A conjugated diene system in a six-numbered ring absorbs at a longer wavelength than the conjugated diene system in an open chain. The λ_{max} resembles that of open-chain trienes, but the intensity is much lower than that observed for open-chain dienes or trienes. Conjugated dienes in a five-membered ring absorb at longer wavelengths with much lower intensities than the open-chain dienes.

The position of the absorption band of conjugated olefins is independent of the solvent because of the nonpolar nature of the hydrocarbon.

The above effects are summarized by the absorption data for conjugated olefins presented in Table V.

An empirical method for determining the bathochromic effect of alkyl substitution in 1,3-butadiene has been formulated by Woodward.[15,16] The introduction of an alkyl group or the formation of an exocyclic double bond causes a bathochromic displacement of about 5 mμ.

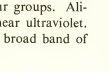
For example, the λ_{max} of allylidenecyclohexane,



can be approximated in the following way. The incorporation of a terminal carbon atom of butadiene

Table V Absorption Data for Conjugated Olefins

COMPOUND	*K*-BAND		SOLVENT
	λ_{max} (mμ)	ϵ_{max}	
1,3-Butadiene	217	20,900	Hexane
1,3,5-Hexatriene	258	35,000	...
1,3-Cyclohexadiene	256	8,000	Hexane
Cyclopentadiene	239	3,400	Hexane

into a cyclohexyl ring is equivalent to two alkyl substituents,  The double bond adjoining the ring is an exocyclic double bond. The approximate λ_{max} of allylidenecyclohexane is, therefore, 217 + (3 × 5) or 232 mμ; the observed λ_{max} for allylidenecyclohexane is 236.5 mμ.

The application of Woodward's rules, in deducing structural detail in steroids, is discussed by Fieser and Fieser.[17]

A *trans* isomer usually has a higher λ_{max} and ϵ_{max} than the corresponding *cis* isomer. The greatest difference is in the intensity of absorption. This difference in the absorption characteristics of *cis* and *trans* isomers is in keeping with the theory that the more elongated a molecule, the more intense is its absorption.

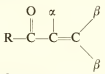
CONJUGATED ENYNES AND DIYNES. Conjugated enynes, such as vinylacetylene, absorb at nearly the same wavelengths as the corresponding conjugated dienes, but the intensity of absorption is much lower. Butadiene absorbs at 217 mμ (ϵ_{max} 20,900); vinylacetylene absorbs at 219 mμ (ϵ_{max} 6400).

Compounds which contain two or three conjugated acetylenic linkages absorb weakly (ϵ_{max} 200–300) in the 220–300 mμ region. The absorption curves are characterized by fine structure. When the number of conjugated acetylenic groups exceeds three, the weak absorption bands move to longer wavelengths and intense bands appear in the short wavelength region of the spectrum. In long-chain polyacetylenes the ϵ value of these bands may exceed 400,000.

CARBONYL CHROMOPHORE IN CONJUGATION. Compounds containing a carbonyl group in conjugation with an ethylenic linkage display a strong *K*-band in the near ultraviolet. The *K*-band falls in the region of 215–250 mμ and has an ϵ_{max} of 10,000–20,000. In

addition to the *K*-band, the α,β-unsaturated carbonyl compounds still display the weak *R*-band of the carbonyl group although it has been displaced to a longer wavelength, 300–350 mμ. Since the carbonyl compounds are polar, the positions of the bands are dependent upon the solvent used. As the polarity of the solvent increases, the λ_{max} of the *K*-band shifts to longer wavelengths whereas λ_{max} of the *R*-band shifts to shorter wavelengths. The two bands are most widely separated in nonpolar solvents such as *n*-hexane.

Woodward has derived empirical generalizations for the effect of substitution upon the position of the *K*-band in the spectra of α,β-unsaturated ketones.[15,16] The positions of the *K*-bands, which result from substitution in the basic formula.



are summarized as follows:

SUBSTITUTION		PROBABLE λ_{max} (mμ)
Unsubstituted		215
α or β	No exocyclic C=C	225
$\alpha\beta$ or $\beta\beta$	No exocyclic C=C	235
$\alpha\beta$ or $\beta\beta$	One exocyclic C=C	240
$\alpha\beta\beta$	No exocyclic C=C	247
$\alpha\beta\beta$	One exocyclic C=C	252

The spectra of α,β-unsaturated aldehydes are similar to those of the α,β-unsaturated ketones. The *R*-bands occur in the 350–370 mμ region and exhibit some fine structure when the spectra are determined in nonpolar solvents.

Absorption data are presented for conjugated ketones and aldehydes in Table VI.

Table VI Absorption Data for Conjugated Ketones and Aldehydes

COMPOUND	*K*-BAND		*R*-BAND		SOLVENT
	λ_{max} (mμ)	log ϵ_{max}	λ_{max} (mμ)	log ϵ_{max}	
Methyl vinyl ketone	212.5	3.85	320	1.43	Ethanol
Methyl isopropenyl ketone	218	3.90	315	1.4	Ethanol
Acrolein	210	4.06	315	1.41	Water
Crotonaldehyde	220	4.17	322	1.45	Ethanol
Crotonaldehyde	214	4.20	329	1.39	Isooctane
			341	1.38	
			352(*s*)	1.25	

(*s*) shoulder.

A strong *K*-band is displayed in the 204–220 mμ region of the near ultraviolet by α,β-unsaturated acids. Substitution of a hydroxyl group, in the α- or β-position of the ethylenic linkage of the α,β-unsaturated carbonyl compounds, results in a marked bathochromic effect.

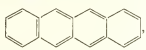
α,β-Diketones, such as biacetyl, show two absorption bands but no *K*-band. The spectrum of biacetyl shows the normal carbonyl absorption at 275 mμ and a series of bands in the 420–450 mμ region.

Benzenoid Systems

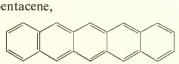
The spectra of benzenoid systems, without chromophoric substitution, are characterized by *B*-bands. *E*-bands appear in the near ultraviolet region of benzene derivatives possessing auxochromic substitution. Conjugated chromophoric substitution results in the appearance of intense *K*-bands in the near ultraviolet region.

The fine structure of the *B*-bands is retained in the spectra of many derivatives of benzene, benzene homologs, and in condensed ring aromatics.

As the number of condensed rings, in a condensed-ring aromatic, increases, the absorption moves to progressively longer wavelengths until absorption occurs in the visible region. Naphthacene,



is yellow; pentacene,



is blue.

ALKYLBENZENES (HYPERCONJUGATION). Alkyl substitution in the benzene ring leads to bathochromic shifts of the *B*-band. The bathochromic effect of hyperconjugation is illustrated by absorption data for alkylbenzenes presented in Table VII.

Table VII Absorption Data for Alkylbenzenes

COMPOUND	λ_{max} (mμ)	ϵ_{max}
Benzene	255	230
Toluene	261	300
1,2,3-Trimethylbenzene	266	360
Hexamethylbenzene	272	300

AUXOCHROMIC SUBSTITUTION (n-π CONJUGATION). The substitution of auxochromic groups in the benzene ring produces marked alterations in the benzene spectrum. The *E*-band and *B*-band are displaced toward longer wavelengths and the *B*-band frequently increases in intensity. The fine structure of the *B*-band is often destroyed, especially when absorption spectra are determined in polar solvents.

The effect of auxochromic substitution is apparent from an examination of spectral data presented in Table VIII.

The data in Table VIII show that the conversion of phenol to the phenolate ion, or aniline to the anilinium ion, causes shifts in λ_{max} of the *B*- and *E*-bands accompanied by changes in ϵ_{max}.

The conversion of phenol to the phenolate ion makes an additional pair of nonbonding electrons available for interaction with the π-electrons of the aromatic nucleus. The availability of this additional pair of nonbonding electrons results in a bathochromic shift of λ_{max} and an increase in ϵ_{max}. When aniline is converted to the anilinium cation, the pair of nonbonding electrons of aniline is no longer available for interaction with the π-electrons of the ring. Consequently, the absorption characteristics of the anilinium cation closely resemble those of benzene.

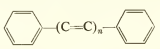
Table VIII Effect of Auxochromic Substitution on the Spectrum of Benzene

COMPOUND	*E*-BAND		*B*-BAND		SOLVENT
	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}	
Benzene	198	8,000	255	230	Cyclohexane
Chlorobenzene	210	7,500	257	170	Alcohol
Thiophenol	236	10,000	269	700	Hexane
Phenol	210.5	6,200	270	1,450	Water
Phenolate anion	235	9,400	287	2,600	Aq. alkali
Aniline	230	8,600	280	1,430	Water
Anilinium cation	203	7,500	254	160	Aq. acid

Confirmation of a suspected phenolic structure may be obtained by comparison of the ultraviolet spectra obtained for the compound in neutral and in alkaline solution (pH 13). Similar confirmatory information for a suspected aniline derivative may be obtained by a comparison of spectra determined in neutral and acid solution (pH 1).

The substitution of a second auxochrome into the benzene nucleus produces additional bathochromic shifts of the absorption bands. The displacement is less for two ortho- or para-directing substituents than for the combination of an ortho- or para-directing substituent with a meta-directing substituent. The displacement is usually greatest when the substitution occurs in the para position. CHROMOPHORIC SUBSTITUTION (π-π CONJUGATION). Chromophoric substitution of benzene gives rise to intense *K*-bands in the same general region where the *E*-bands are observed for auxochromic substituted benzenes (200–250 mμ). The *K*-band of styrene, for example, is at 244 mμ.

A solution of biphenyl, in alcohol, shows a strong absorption band at 250 mμ (ϵ_{max} 18,000) due to conjugation between the two rings. In diphenylmethane, in which the two aromatic rings are no longer in conjugation, the value of ϵ_{max} drops to about twice that of a single benzene nucleus. The diphenyl polyenes,



show high-intensity *K*-bands. The wavelength and intensity of absorption of diphenyl polyenes increase with the increase in length of the conjugated chain.

The spectra of chromophoric substituted benzenes may consist of *K*-bands, *B*-bands, and *R*-bands. The *B*-bands lose their fine structure. *R*-bands are observed only in those cases in which the chromophore itself absorbs in the near ultraviolet—benzaldehyde or acetophenone. In the spectra of compounds such as phenyl cyanide and benzoic acid, intense *K*-bands are observed along with the *B*-bands. The nitrile and carboxyl groups are transparent but are able to exert a chromophoric effect upon benzene.

Examples of the absorption characteristics of benzene derivatives, containing chromophoric groups, are presented in Table IX.

The occurrence of more complex chromophoric groups in conjugation with the benzene nucleus sometimes brings the *E*-bands into the near ultraviolet region. Strong *K*-bands, shifted to the longer wavelengths, usually swamp the *B*-bands. *R*-bands may be observed at longer wavelengths.

The effect of complex chromophoric substitution is evident from the data presented in Table X.

Heteroaromatics

Saturated heterocyclic compounds are transparent at wavelengths above 200 mμ. The common five-membered ring heteroaromatics, such as furan, thiophene, pyrrole,

Table IX Absorption Characteristics of Chromophoric Substituted Benzenes

COMPOUND	*K*-BAND		*B*-BAND		*R*-BAND		SOLVENT
	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}	
Benzene	...	...	255	215	...	...	Alcohol
Styrene	244	12,000	282	450	...	...	Alcohol
Phenylacetylene	236	12,500	278	650	...	...	Hexane
Benzaldehyde	244	15,000	280	1,500	328	20	Alcohol
Acetophenone	240	13,000	278	1,100	319	50	Alcohol
Nitrobenzene	252	10,000	280	1,000	330	125	Hexane
Benzoic acid	230	10,000	270	800	...	...	Water
Phenyl cyanide	224	13,000	271	1,000	...	...	Water

Table X Absorption Characteristics of Monosubstituted Benzene Derivatives–Complex Chromorphoric Substitution

COMPOUND	*E*-BAND		*K*-BAND		*R*-BAND		SOLVENT
	λ_{max} (μ)	ϵ_{max}	λ_{max} (μ)	ϵ_{max}	λ_{max} (μ)	ϵ_{max}	
Diphenyl	...	...	246	20,000	...	...	Hexane
Benzophenone	...	...	252	20,000	325	180	Alcohol
Benzylidene acetone	220	12,000	286	25,000	...	...	Alcohol
Azobenzene	...	...	319	19,500	445	300	Alcohol

and thiazole, possesses conjugated unsaturation. In contrast to the acyclic dienes which display only strong *K*-bands, these structures show both *K*- and *B*-bands. The *K*-bands appear in the region near 200–210 mμ (ϵ_{max} 5000–16,000). The *B*-bands display fine structure similar to the isocyclic aromatics.

The absorption characteristics of some common five-membered-ring heteroaromatic compounds are presented in Table XI.

Table XI Absorption Characteristics of Common Heteroaromatic Compounds (Five-Membered Ring)

COMPOUND	*B*-BAND		SOLVENT
	λ_{max} (μ)	ϵ_{max}	
Furan	252	1	*n*–Hexane
Thiophene	231	5,620	*n*–Hexane
Pyrrole	240	302	*n*–Hexane
Thiazole	240	4,000	*n*–Hexane

When chromophoric substitution occurs on the heteroaromatic ring, the *B*-band disappears and *E*- and *K*-bands appear in the near ultraviolet. The bathochromic and hyperchromic effects resulting from chromophoric substitution of some heteroaromatic compounds, containing five-membered rings, are shown in Table XII.

Table XII Absorption Characteristics of Chromophoric Substituted Heteroaromatics (Five-Membered Ring)

COMPOUND	*E*-BAND		*K*-BAND		SOLVENT
	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}	
Furfural	227	2,228	272	13,180	Alcohol
2-Acetylfuran	225	2,400	269	13,500	Alcohol
2-Acetylthiophene	260	7,760	285	5,620	Alcohol
2-Acetylpyrrole	250(*s*)	4,370	287	15,900	Alcohol
2-Furylacrylic acid	230	1,780	300	22,900	Alcohol

(*s*) shoulder.

Heteroaromatic ketones and aldehydes do not show an *R*-band.

The six-membered heteroaromatics display a *B*-band resembling those of the isocyclic aromatics. The *B*-bands fall at essentially the same position as those of the corresponding isocyclic aromatics but are usually more intense. The *B*-bands display vibrational fine structure especially when the spectra are determined in nonpolar solvents.

The absorption characteristics of some heteroaromatic compounds containing nitrogen are presented in Table XIII.

Table XIII Absorption Characteristics of Heteroaromatic Compounds Containing Nitrogen (Six-Membered Ring)

COMPOUND	*K*-BAND*		*B*-BAND*		SOLVENT
	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}	
Pyridine	...	...	250	2,000	Hexane
2-Methylpyridine	...	...	262	2,340	Isooctane
3-Methylpyridine	...	...	257	2,140	Isooctane
4-Methylpyridine	...	...	251	2,240	Isooctane
Pyrazine	...	...	260	5,600	Hexane
Quinoline	275	3,700	313	2,700	Cyclohexane
Iso-Quinoline	265	3,980	317	3,470	Cyclohexane
Acridine	250	107,000	355	10,500	Alcohol

* Most intense peak of fine structure.

The fine structure of the *B*-band of pyridine and its alkyl derivative disappears when the spectra are determined in acidic media. The resulting *B*-band has about twice the intensity of the *B*-band observed in neutral solvents. The hyperchromic effect probably results from the introduction of a positive charge on the nitrogen atom.

Chromophoric substitution in pyridine results in the appearance of a strong *K*-band in the near ultraviolet and a bathochromic shift of the *B*-band. The ultraviolet spectrum of 3-acetylpyridine displays a *K*-band at 227 mμ (ϵ_{max} 9300) and a *B*-band at 267 mμ (ϵ_{max} 2460), when determined in neohexane.

References

1. Gillam, A. E., and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold, London, 2nd ed., 1957.
2. Braude, E. A., "Ultraviolet and Visible Light Absorption," Chapter 4, pp. 131–94, in *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955.
3. Braude, E. A., "Ultra-Violet Light Absorption and the Structure of Organic Compounds," *Ann. Repts. on Progress Chem.*, Chemical Society of London, Vol. XLII (1945), pp. 105–30.
4. Duncan, A. B. F., and F. A. Matsen, "Electronic Spectra in the Visible and Ultraviolet," Vol. IX, pp. 581–706, in *Technique of Organic Chemistry*, A. Weissberger, ed., Interscience, New York, 1956.
5. Bauman, R. P., *Absorption Spectroscopy*, John Wiley, New York, 1962.
6. Jaffé, H. H., and Milton Orchin, *Theory and Application of Ultraviolet Spectroscopy*, John Wiley, New York, 1962.

7. "Electronic Spectral Data," Vol. I, M. J. Kamlet, ed., Interscience, New York, 1960. Covers literature 1946–1952.
8. "Electronic Spectral Data," Vol. II, H. G. Ungnade, ed., Interscience, New York, 1960. Covers literature 1953–1955.
9. Friedel, R. A., and Milton Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley, New York, 1951. Revised ed., 1958.
10. *Catalog of Ultraviolet Absorption Spectrograms*, American Petroleum Institute Project 44, Carnegie Institute of Technology, Pittsburgh, Penn.
11. *Ultraviolet Spectral Data*, Manufacturing Chemists Association Research Project, Carnegie Institute of Technology, Pittsburgh, Penn.
12. Hershenson, H. M., *Ultraviolet Absorption Spectra*, Index for 1954–1957, Academic Press, New York, 1959.
13. Láng, L., *Absorption Spectra in the Ultraviolet and Visible Region*, Academic Press, New York, 1961.
14. "Spectrometry Nomenclature," *Anal. Chem.*, **33**, 1968 (1961).
15. Woodward, R. B., *J. Am. Chem. Soc.*, **63**, 1123 (1941).
16. Woodward, R. B., ibid., **64**, 72, 76 (1942).
17. Fieser, L. M., and Fieser, M., *Natural Products Related to Phenanthrene*, Reinhold, New York, 1949, p. 184 ff.

CHAPTER SIX

Sets of Spectra Translated into Compounds

In practice, identification of an organic compound begins with a history, and large areas are quickly excluded from further consideration. To put our methodology to a rigorous test, we shall dispense with the sample history. The limits will be set as follows: The samples are quite pure; they may contain carbon, hydrogen, oxygen, nitrogen, sulfur, and the halogens in any combination; since our table of isotope contribution runs only to a molecular weight of 250, the samples will be limited to this range.

Within these restrictions, we can still cover a vast expanse of organic chemistry. The two major areas we have arbitrarily excluded in our selection of samples are silicon and phosphorus chemistry. These are rather specialized fields, and it is hardly likely that an analytical chemist would encounter a silicon- or phosphorus-containing compound without prior knowledge that these elements were present.

We are operating under one more handicap. Under realistic conditions, we would have access to a library of reference spectra; but we shall make structural assignments using only the brief charts and tables given in this book.

Our first step in every case is to attempt to establish an empirical formula from the parent mass and the isotope contributions. In a number of cases, the parent peak

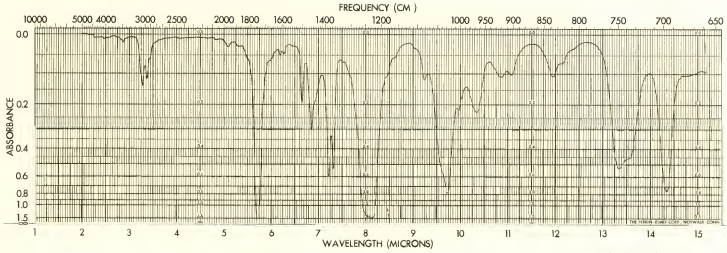
is so small that the isotope contributions cannot be accurately measured. We settle for the molecular weight. In some cases, the parent peak may be missing. We then try to establish the molecular weight from other evidence. In many cases this can be done from the fragmentation pattern and from the other spectra at hand. In other cases, we may resort to preparation of appropriate derivatives, to other methods of obtaining molecular weights, or to other methods of determining elemental composition.

There is no prescribed procedure beyond this point; nor is there any substitute for experience gained through practice. We shall use the obvious features of one spectrum to bring out the more subtle aspects of another. The mental processes involve formulation of possibilities, weighing of evidence, elimination of possibilities, and selection of the most likely candidate; confirmation is obtained by synthesis or by agreement with the literature. Let us work through the twenty samples comprising this chapter.

We may not always come up with an unequivocal structure; nor do we in any system of organic analysis. However, we should at least be able to narrow down the possibilities to several structures (often isomers) and to indicate the steps required to complete the identification.

Mass spectra were obtained on the Consolidated Electrodynamics Corporation Model 21-103C. The lower limit of the fragmentation patterns was mass 26. Peaks of less than 3% relative intensity were not reported except for the parent and isotope peaks. Infrared spectra were run on the Perkin-Elmer Corporation Model 221. NMR spectra were run on the Varian Associates Model A-60; samples were dissolved in carbon tetrachloride or deuterated chloroform, and 1% tetramethylsilane in the solution was used as a reference. Ultraviolet spectra were obtained from the literature, or were run on Applied Physics Corporation's Cary Model 14M at pH 7, pH 1, and pH 13. Only the pH 7 spectrum is recorded unless a change occurred at pH 1 or pH 13.

Infrared Spectrum *Compound 6-1*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	6.	77	22.
38	5.	78	6.
39	20.	79	26.
41	4.	89	13.
42	3.	90	47.
43	73.	91	71.
50	11.	92	6.
51	23.	105	6.
52	6.	106	3.
62	3.	107	20.
63	9.	108	100.
64	3.	109	8.
65	18.	150	28.70
		151	2.84
		152	0.26

ISOTOPE ABUNDANCES

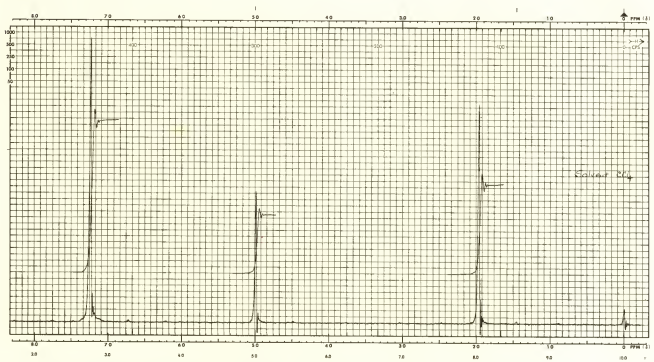
m/e	% of *P*
150 (*P*)	100.
151 (*P* + 1)	9.9
152 (*P* + 2)	0.9

Ultraviolet Data

λ_{max}^{EtOH}	ϵ_{max}
268	101
264	158
262	147
257	194
252	153
248 (*s*)	109
243 (*s*)	78

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER I

The first step in translating these four spectra into a molecular structure is to establish an empirical formula. The parent peak is 150; thus, we have the molecular weight. The parent peak is an even number. We are, therefore permitted either no nitrogen atoms, or an even number of them. The $P + 2$ peak obviously does not allow for the presence of sulfur or halogen atoms.

We now look in Appendix A of Chapter 2 under molecular weight 150. We are faced with 29 empirical formulas of molecular weight 150 containing only CHN and O. Our $P + 1$ peak is 9.9% of the parent peak. We list the empirical formulas whose calculated isotopic contribution to the $P + 1$ peak falls—to be arbitrary—between 9.0 and 11.0; we also list their $P + 2$ values:

FORMULA	$P + 1$	$P + 2$
$C_7H_{10}N_4$	9.25	0.38
$C_8H_8NO_2$	9.23	0.78
$C_8H_{10}N_2O$	9.61	0.61
$C_8H_{12}N_3$	9.98	0.45
$C_9H_{10}O_2$	9.96	0.84
$C_9H_{12}NO$	10.34	0.68
$C_9H_{14}N_2$	10.71	0.52

We immediately eliminate three of these formulas because they contain an odd number of nitrogen atoms. The $P + 2$ peak is 0.9% of the parent; this best fits $C_9H_{10}O_2$, which we shall tentatively designate as our empirical formula. We make a mental note that both the intensity of the parent peak, and the C-to-H ratio of the empirical formula indicate aromaticity.

We turn now to the infrared spectrum and note the C=O band at about 1745 cm^{-1} (5.73 μ). This, together with the presence of two O atoms in the empirical formula, suggests an ester. We look for confirmation in the C—O—C stretching region and note the large broad band at about 1225 cm^{-1} (8.15 μ) characteristic of an acetate. Two large bands at about 749 cm^{-1} (13.35 μ) and 697 cm^{-1} (14.35 μ) suggest a singly substituted benzene ring.

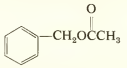
We have tentatively established the presence of a benzene ring and are quite confident about the acetate group. Furthermore, we note from the position of the carbonyl band that the C=O moiety is not conjugated with the ring. This is confirmed by the wavelengths and intensities of the ultraviolet absorption peaks which also eliminate a ketone from consideration. If we subtract a singly substituted benzene ring and an acetate group from the empirical formula we arrive at the following:

$$\text{empirical formula} \longrightarrow C_9H_{10}O_2$$

$$C_6H_5 + CH_3\overset{\overset{O}{\|}}{C}—O \longrightarrow C_8H_8O_2$$

$$\text{remaining} \longrightarrow CH_2$$

It takes no great imagination to insert the CH_2 between the ring and the acetate group, and write



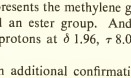
The NMR spectrum provides almost conclusive confirmation for the above structure. We see three sharp unsplit peaks in the following positions and with the following integrated intensities

τ	δ	INTENSITY
2.78	7.22	5
5.00	5.00	2
8.04	1.96	3

The five protons at δ 7.22, τ 2.78, of course, are the five benzene-ring protons. The singlet of two protons at δ 5.00, τ 5.00 represents the methylene group substituted by a phenyl and an ester group. And, of course, the singlet of three protons at δ 1.96, τ 8.04 represents the methyl group.

We can obtain additional confirmation by returning to the mass spectrum and considering the fragmentation pattern (see Appendix B, Chapter 2) in view of the information at hand. The base peak at 108 is a rearrangement peak representing cleavage of an acetyl group (43) and rearrangement of a single hydrogen atom. The large peak at mass 91 is the benzyl (or tropylium) ion formed by cleavage beta to the ring. And the large peak at mass 43, of course, represents the acetyl fragment. The peaks at 77, 78, and 79 are additional evidence for the benzene ring.

We can state with a high degree of confidence that the compound represented by these spectra is:



Benzyl acetate

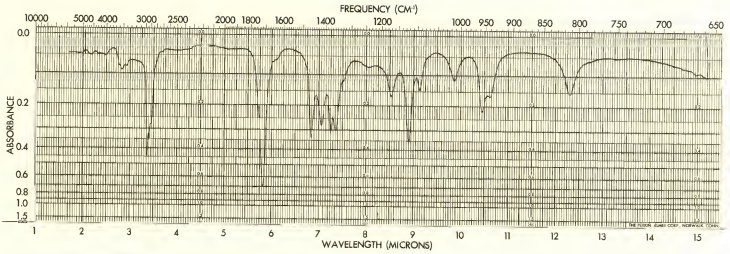
There are, of course, a number of other sequences through which we might arrive at the identity of this compound. Having established the empirical formula,

we could note at once the characteristic benzene ring peak at δ 7.22, τ 2.78, in the NMR spectrum. We could confirm this by the typical "benzenoid" fine-structure absorption in the ultraviolet spectrum. The base peak in the mass spectrum is treacherous because it is a rearrangement peak, but the mass 91 peak immediately calls to mind the benzyl (or tropylium) structure. The large mass 43 peak strongly suggests the CH_3CO group in view of the C=O peak in the infrared. Subtraction of a benzyl and an acetyl group from the empirical formula leaves a mass of 16; consideration of the infrared spectrum leaves very little question as to how to handle this oxygen atom.

The student will find it instructive to write the possible isomeric structures and to eliminate them on spectrometric grounds.

Infrared Spectrum

Compound 6-2



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak
26	11.
27	39.
29	92.
39	4.
41	3.
42	5.
43	3.
56	5.
57	100.
58	4.
86	18.5
87	1.15
88	0.074

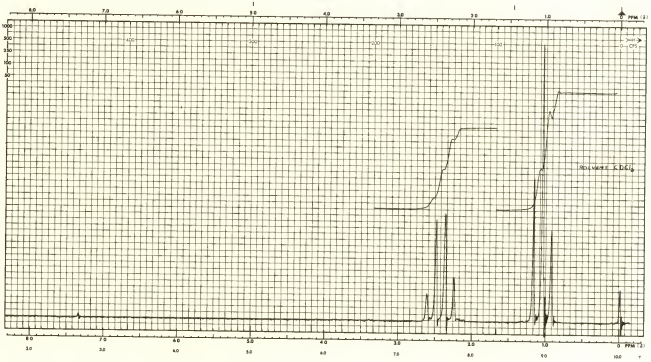
ISOTOPE ABUNDANCES

m/e	% of *P*
86 (*P*)	100.
87 (*P* + 1)	6.2
88 (*P* + 2)	0.4

Ultraviolet Data

λ_{max}^{EtOH}	$\log \epsilon_{max}$
273	1.31

NMR Spectrum (*Solvent CDCl*$_3$)



COMPOUND NUMBER 2

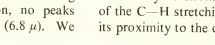
The parent peak in the mass spectrum is 86, and the $P + 1$ peak is 6.2% of the parent peak. We look under molecular weight 86 in Appendix A of Chapter 2 and list the empirical formulas whose calculated $P + 1$ peak value falls between, say, 4.8 and 6.7. We can eliminate formulas containing an odd number of nitrogen atoms.

FORMULA	$P + 1$	$P + 2$
$C_4H_{10}N_2$	5.25	0.11
$C_5H_{10}O$	5.60	0.33
C_6H_{14}	6.71	0.19

Our $P + 2$ peak is 0.4% of the parent. This best fits $C_5H_{10}O$ which we tentatively adopt as the empirical formula. Neither sulfur nor a halogen is permitted.

The C-to-H ratio of the empirical formula points to an aliphatic structure. This deduction is supported by the general aspect of the infrared spectrum: lack of strong absorption in the long wavelength region, no peaks between 1665 cm^{-1} (6.0 μ) and 1470 cm^{-1} (6.8 μ). We may note, however, that the C—H stretching peak at 2975 cm^{-1} (3.37 μ) is rather close to the high-frequency limit assigned to alkyl C—H stretching peaks. We glance at the NMR spectrum and confirm the absence of aromatic or olefinic protons.

The conspicuous feature of the infrared spectra is the strong carbonyl peak at 1715 cm^{-1} (5.83 μ). We are limited, essentially, to a ketone or an aldehyde by the empirical formula. The low-intensity peak at 273 mμ in the ultraviolet spectrum is at a rather short wavelength for an aldehyde and favors a ketone. Neither the infrared (absence of aldehyde C—H stretching peak), nor the NMR (no aldehyde proton) supports the aldehyde structure. We may now write $(C_4H_{10})C{=}O$ and consider a choice of isomers. This is resolved very readily in the NMR spectrum by the characteristic triplet-quartet signifying an ethyl group. We are forced to write the symmetrical structure.

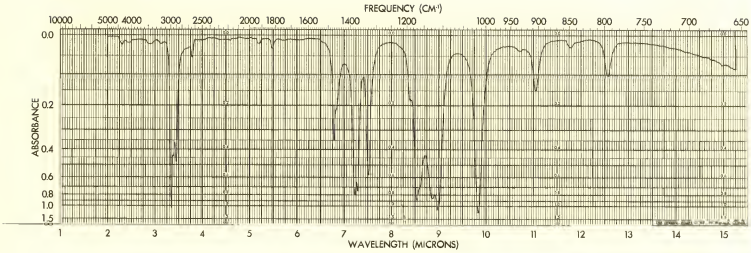


3-Pentanone
or
Diethyl ketone

The fragmentation pattern of the mass spectrum is consonant with this structure. The base peak at mass 57 denotes the highly probable α-cleavage with charge retention on the oxygenated fragment. The peak of almost equal intensity at mass 29 results from the same cleavage but with charge retention on the alkyl moiety.

The only worrisome point was the rather high frequency of the C—H stretching peak. This is now explicable by its proximity to the carbonyl group.

Infrared Spectrum *Compound 6-3*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak
26	3.
27	18.
29	6.
31	4.
39	11.
41	17.
42	6.
43	61.
44	4.
45	100.
59	11.
87	21.
102	0.63
103	0.049
104	0.0032

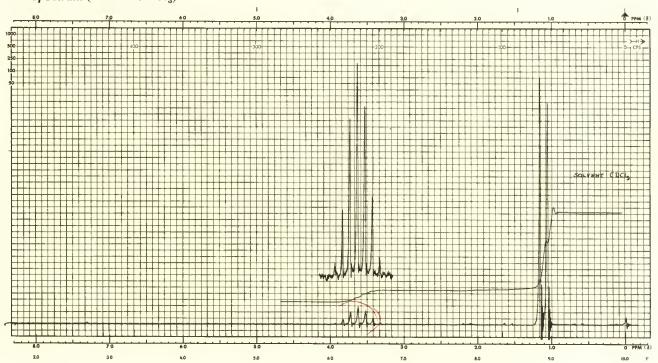
ISOTOPE ABUNDANCES

m/e	% of *P*
102 (*P*)	100.
103 (*P* + 1)	7.8
104 (*P* + 2)	0.5

Ultraviolet Data

transparent above 200 mμ

NMR Spectrum (*Solvent* $CDCl_3$)



COMPOUND NUMBER 3

In accordance with our usual procedure, we write the possible empirical formulas (together with the $P + 1$ and $P + 2$ peaks) under the molecular weight, in this case, 102:

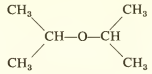
FORMULA	$P + 1$	$P + 2$
$C_6H_{14}N_2$	6.39	0.17
$C_6H_2N_2$	7.28	0.23
$C_6H_{14}O$	6.75	0.39
C_7H_2O	7.64	0.45
C_8H_6	8.74	0.34

The best fit to our $P + 1$ (7.8) and $P + 2$ (0.5) values is C_7H_2O. But this is a trivial formula as is $C_6H_2N_2$. The next best fit is $C_6H_{14}O$. We shall proceed on this basis. Sulfur or halogen is not permitted.

The compound is aliphatic on the basis of the C-to-H ratio, the general appearance of the IR spectrum (though as in Compound Number 2, the C—H stretch is at rather a high frequence), the lack of absorption in the ultraviolet spectrum, and the absence of peaks at low field in the NMR spectrum.

There is no carbonyl or hydroxyl absorption in the infrared spectrum. Since the empirical formula requires an oxygen atom, we consider some type of ether, and look for C—O absorption which we find at 1112 cm^{-1} (8.99 μ).

The NMR spectrum is quite definitive. The doublet and the symmetrical heptet in the integrated ratio of 6 : 1 spell out an isopropyl group. Obviously the molecule is symmetrical about the oxygen atom. We write:

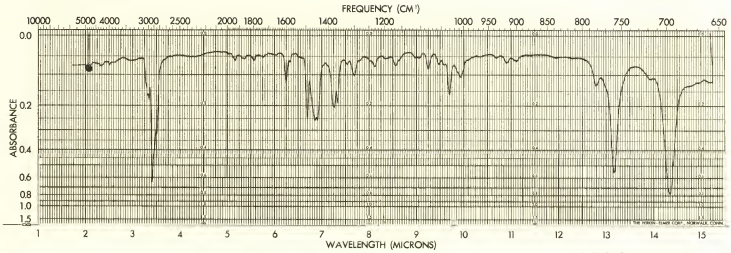


Diisopropyl ether

The infrared doublet at 1380 cm^{-1} (7.23 μ) and 1370 cm^{-1} (7.28 μ) confirms the isopropyl group. The rather high-frequency C—H stretching peak is explained by the presence of the oxygen atom.

The base peak (45) in the mass spectrum results from α- and β-cleavage with rearrangement of a hydrogen atom. This is prominent in α-substituted ethers. Removal of a methyl group (β-cleavage) accounts for the mass 87 peak. α-Cleavage with retention of the charge on the alkyl portion results in the large mass 43 peak.

Infrared Spectrum *Compound 6-4*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	9.	92	6.
29	6.	103	9.
39	7.	104	5.
41	13.	105	26.
50	5.	115	5.
51	11.	117	5.
55	4.	118	4.
63	4.	119	100.
65	5.	120	10.
77	13.	133	4.
78	6.	148	16.20
79	9.	149	1.98
91	60.	150	0.13

ISOTOPE ABUNDANCES

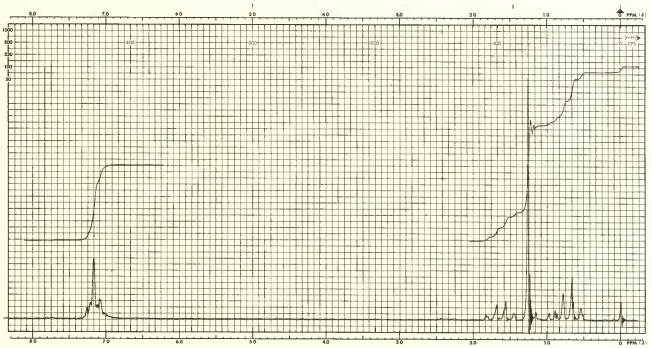
m/e	% of *P*
148 (*P*)	100.
149 (*P* + 1)	12.22
150 (*P* + 2)	0.80

Ultraviolet Data

$\lambda^{\text{Isooctane}}_{\text{max}}$	$\log \epsilon_{\text{max}}$
217 (*s*)	3.60
236 (*s*)	1.57
242 (*s*)	1.85
247.5 (*s*)	2.09
252.5	2.19
258	2.29
261	2.20
264	2.18

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 4

The parent peak in the mass spectrum is 148. $P + 1$ is 12.22%, and $P + 2$ is 0.80%. We write the possible empirical formulas (together with the $P + 1$ and $P + 2$ peaks) omitting those with an odd number of N atoms.

FORMULA	$P + 1$	$P + 2$
$C_{10}H_{12}O$	11.04	0.75
$C_{11}H_{16}$	12.14	0.67
$C_{12}H_4$	13.03	0.78

If we allow for a reasonable range of error in the $P + 1$ and $P + 2$ peaks, any of the preceding formulas fits our data. We can eliminate $C_{12}H_4$ as trivial. Neither sulfur nor halogen is present.

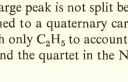
The infrared spectrum shows a strong peak at 759 cm^{-1} (13.17 μ) and another at 696 cm^{-1} (14.35 μ). We immediately think in terms of a monosubstituted benzene ring. This impression is reinforced by the small C—H stretching peak (triplet?) at 3030–2985 cm^{-1} (3.30–3.35 μ) and by the peak at 1600 cm^{-1} (6.25 μ) and at 1493 cm^{-1} (6.70 μ). There is no evidence for a carbonyl group, a hydroxyl group, or an ether bond. In addition to the benzene ring, there appears to be a substantial amount of aliphatic character as evidenced by the strong aliphatic C—H stretching peak at 2925 cm^{-1} (3.42 μ).

The "benzenoid" type absorption in the ultraviolet and the low field absorption in the NMR spectrum provide additional confirmation for the presence of an aromatic ring. We have not completely ruled out $C_{10}H_{12}O$, because we can still consider a furan ring, although the position of the NMR low-field peak is better for a benzene ring. We rather lean toward $C_{11}H_{16}$ and write the semistructural formula

Let us consider the fragmentation pattern. The base peak is 119, which corresponds to C_9H_{11}. Assuming the usual cleavage beta to the ring, we write

The large singlet at δ 1.25, τ 8.75 accounts for the six methyl protons if we assign five protons to the benzene ring peak. The large peak is not split because the methyl groups are attached to a quaternary carbon atom.

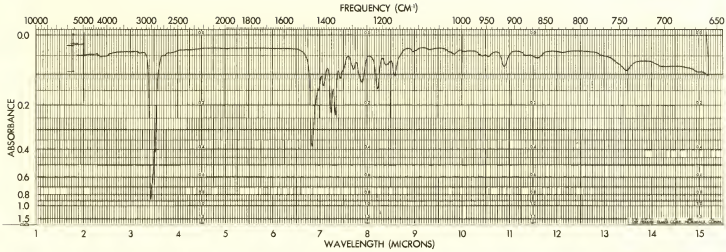
We are left with only C_5H_5 to account for; we scarcely need the triplet and the quartet in the NMR spectrum to lead us to write



t-Amylbenzene

We overlook several minor peaks in the NMR spectrum as evidence of small amounts of an impurity. The fragmentation peaks in the mass spectrum at mass 77, 78, and 79 are familiar. The large peak at 91 is the sometimes unreliable benzyl or tropylium peak, in this case obviously a rearrangement peak, as is the mass 105 peak. The pair of peaks in the infrared spectrum at 1377 cm^{-1} (7.26 μ) and 1361 cm^{-1} (7.35 μ) is similar to that expected from a *t*-butyl group.

Infrared Spectrum **Compound 6-5**



Cell thickness 0.01 *mm*

***Mass Spectral Data* (*Relative Intensities*)**

m/e	% of base peak	*m/e*	% of base peak
27	21.	70	6.
29	20.	71	61.
39	10.	72	4.
41	28.	79	5.
42	4.	87	4.
43	100.	101	5.
44	4.	102	4.
45	6.	103	3.
47	5.	136	11.
57	3.	206	25.90
59	4.	207	3.24
69	7.	208	2.48

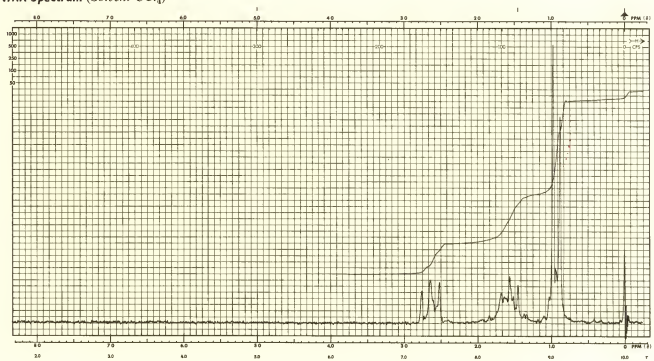
ISOTOPE ABUNDANCES

m/e	% of *P*
206 (*P*)	100.
207 (*P* + 1)	12.5
208 (*P* + 2)	9.6

Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
248	2.55

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 5

Following our usual practice, we strike immediately for the parent peak (206) and start to list possibilities under that molecular weight. But consideration of the $P + 2$ peak brings us up short. Obviously, we are no longer dealing with compounds containing only C, H, O, and N. The $P + 2$ peak is too small for a chlorine or a bromine atom (see Table II, Chapter 2) and too large for a sulfur atom. But it will accommodate two sulfur atoms very nicely.

We subtract the mass of two sulfur atoms from 206 and get 142, which is the weight of the rest of the molecule. We now compile the list of possibilities from the table under 142, using the $P + 1$ peak (and, of course, the fact that 142 is an even number) to narrow the possible empirical formulas. The $P + 1$ peak becomes 12.5 minus 2×0.78 which gives 10.9; this removes the contribution of the two S^{33} atoms.

FORMULA	$P + 1$
$C_{10}H_6O$	10.94
$C_{10}H_{22}$	11.16
$C_{11}H_{10}$	12.05

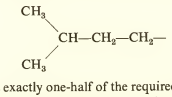
The infrared and the NMR spectra convey a strong impression that we are dealing with an aliphatic compound. The ultraviolet spectrum is not especially informative. The infrared gives no evidence for the presence of an oxygen atom; in fact, it is rather featureless save for the strong aliphatic C—H stretching bands at 2915–2841 cm^{-1} (3.43–3.52 μ), the CH_2 and CH_3 bending vibration at 1464 cm^{-1} (6.83 μ), and the twin peaks at 1381 and 1364 cm^{-1} (7.24 and 7.33 μ), which we may often associate with chain branching.

Although $C_{11}H_{10}$ is a possible empirical formula, we can find no support for unsaturated character. We find no evidence for the presence of oxygen, so we write $C_{10}H_{22}S_2$ as our empirical formula.

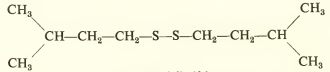
The base peak, mass 43, in the mass spectrum allows us to write $CH_3CH_2CH_2$ or CH_3CHCH_3. We choose the latter for several reasons. A base peak is more likely to result from cleavage at a branch. The large doublet in the NMR spectrum is familiar as the methyl protons of an isopropyl group. We also associated a pair of peaks in the infrared spectrum with chain branching.

We note a slightly distorted triplet in the NMR spectrum centered on δ 2.65, τ 7.35. This represents two protons (possibly CH_2) if we assign six protons to the large methyl doublet. A sulfur atom adjacent to the methylene group would account for its downfield shift.

If we examine the multiplet in the NMR spectrum centered at about δ 1.55, τ 8.45, we can pick out a triplet whose components peaks have the same spacing as those of the triplet further downfield. However, the integration shows that the multiplet contains three protons. It cannot be a methyl group because that would have produced a quartet rather than a triplet at the downfield position. It must then be another methylene and contain the CH group whose proton is responsible for producing the large doublet upfield. The extraneous peaks in and around the triplet at δ 1.55, τ 8.45 must then belong to the CH proton. We now have enough information to write



Since this is exactly one-half of the required weight of the alkyl portion, we may exercise a modicum of chemical sense and write the full structure

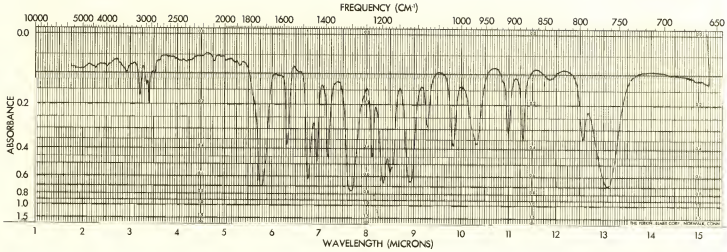


Diisoamyl disulfide

The fragmentation pattern, although complex, bears this structure out. The large peak at 71 represents cleavage α to the sulfur with retention of the charge on the alkyl fragment. The peak at 136 results from the same cleavage with shift of a hydrogen atom to the sulfur-containing fragment which retains the charge.

We have not rigorously proved that the two sulfur atoms are contiguous, although the ultraviolet spectrum supports the disulfide structure. But it would be difficult to write another structure to fit the spectra. We could carry out reductive cleavage and obtain conclusive spectral data on the resulting mercaptan.

Infrared Spectrum *Compound 6-6*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak
27	4.
29	9.
37	7.
38	12.
39	28.
53	3.
67	3.
68	6.
95	100.
96	8.
126	31.95
127	2.24
128	0.26

ISOTOPE ABUNDANCES

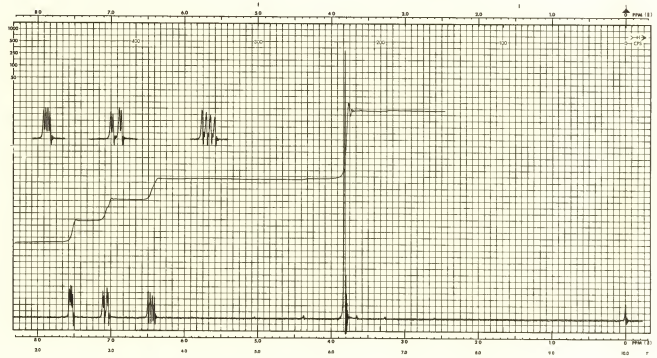
m/e	% of *P*
126 (*P*)	100.
127 (*P* + 1)	7.02
128 (*P* + 2)	0.81

Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
220.0(*s*)	3.47
250.5	4.13

(*s*) = shoulder

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 6

The following empirical formulas fit our data for the parent peak and the $P + 1$ peak:

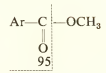
FORMULA	$P + 1$	$P + 2$
$C_5H_6N_2O_2$	6.34	0.57
$C_5H_{10}N_4$	7.09	0.22
$C_6H_6O_3$	6.70	0.79
$C_6H_{10}N_2O$	7.45	0.44

The formula that best fits our $P + 2$ peak is $C_6H_6O_3$. We should bear in mind, however, that the $P + 2$ peak may be higher than the calculated figure, and we accept $C_6H_6O_3$ only as a tentative formula.

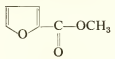
The empirical formula and the general appearance of the infrared spectrum suggest aromaticity. We note strong peaks beyond 800 cm^{-1} (12.5 μ), two strong peaks at 1587 cm^{-1} (6.30 μ) and 1435 cm^{-1} (6.95 μ), and a medium peak at 3106 cm^{-1} (3.22 μ). The intense band in the ultraviolet spectrum at 250 mμ is suggestive of a chromophore conjugated with an aromatic ring. The striking pattern at the low-field end of the NMR spectrum demands an aromatic ring of some sort.

A conspicuous feature of the infrared spectrum is the C=O peak at 1730 cm^{-1} (5.78 μ). Bearing in mind that we are probably dealing with a conjugated chromophore, we can make a choice between a ketone and an ester. We lean toward an ester because the conjugated ketone C=O bands are usually at lower frequency. We also look in vain for the long wavelength *R*-band of conjugated ketones in the ultraviolet spectrum. (We should recall, however, that heteroaromatic ketones do not show a detectable *R*-band). There are a number of strong bands between 1420 and 1110 cm^{-1} (7.05 and 9.0 μ) some of which may be associated with an ester C—O absorption. And, of course, the empirical formula permits an ester group plus another oxygen.

Now we can profitably consider the base peak, mass 95, in the mass spectrum. The base peak arises from a loss of mass 31, and this loss is practically diagnostic for a methyl ester. We can write



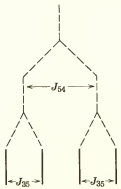
The mass 95 component then must be $C_4H_3O—C=O$, and we write the structural formula



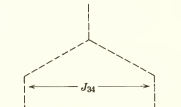
Methyl-2-furoate

The NMR spectrum is nicely in accord with this structure. We see three separate ring-protons at low field, and the three protons of the methyl group as a sharp singlet at δ 3.81, τ 6.19. From low to high field, the three low-field peaks (multiplets) represent the five-proton, the three-proton, and the four-proton, respectively. Each is shifted downfield, by the carboxylate substituent, from its position in an unsubstituted furan ring, the three-proton being most strongly affected.

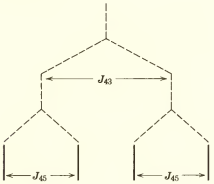
These multiplets afford a tidy demonstration of spin-spin coupling. The system is *AMX* with three coupling constants. The five-proton is coupled with the four-proton ($J_{54} = 4$ cps) and with the three-proton ($J_{53} = 2$ cps). The five-proton, therefore, shows two pairs of peaks.



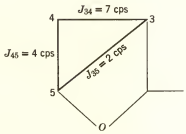
The three-proton is coupled with the four-proton ($J_{34} = 7$ cps) and with the five-proton ($J_{35} = 2$ cps). The three-proton, thus, shows two pairs.



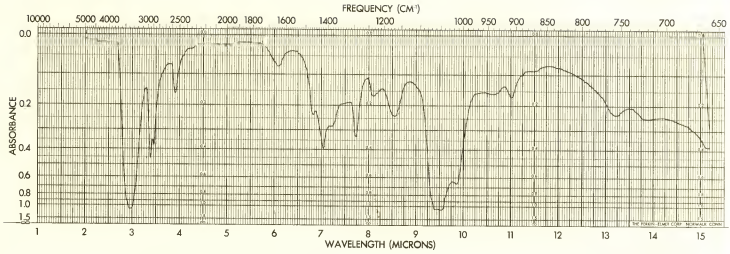
The four-proton is coupled with the three-proton ($J_{43} = 7$ cps) and with the five-proton ($J_{45} = 4$ cps). Again we see two pairs.



The couplings can be summed up as follows:



Infrared Spectrum *Compound 6-7*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	11.	46	25.
27	33.	47	100.
28	6.	48	65.
29	28.	49	10.
31	64.	50	3.
32	9.	57	6.
33	12.	58	11.
34	8.	59	36.
35	7.	60	98.
42	7.	61	7.
43	24.	62	5.
44	21.	78	34.
45	58.	79	1.18
		80	1.7

ISOTOPE ABUNDANCES

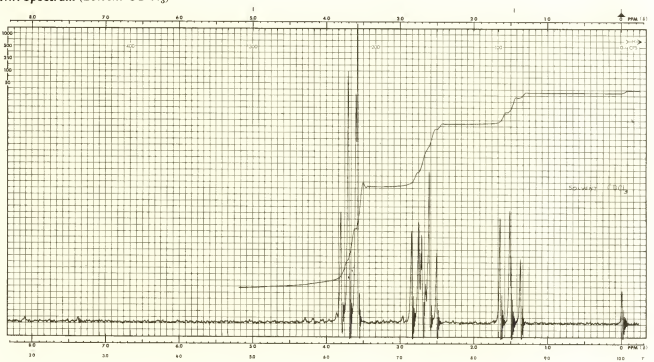
m/e	% of *P*
78 (*P*)	100.
79 (*P* + 1)	3.48
80 (*P* + 2)	5.0

Ultraviolet Data

λ_{infl}^{EtOH}	ϵ_{infl}
232	136

infl = inflection.

NMR Spectrum (*Solvent* $CDCl_3$)



COMPOUND NUMBER 7

We immediately note the large $P + 2$ peak which suggests that one sulfur atom is present. We then list the possible empirical formulas under mass 46 (78–32). We should list all except the trivial formulas and those containing an odd number of N atoms; we also subtract 0.78 from the $P + 1$ peak, which leaves 2.70. But this turns out to leave us with only a single choice, C_2H_6O. The empirical formula, therefore, is C_2H_6OS.

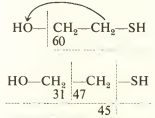
The infrared spectrum shows a strong, rather broad band at 3367 cm^{-1} (2.97 μ). Our impression is that we are dealing with an alcohol, and the very broad band at about 1050 cm^{-1} (9.5 μ) suggests a primary alcohol. Our attention is then caught by a rather weak band at 2558 cm^{-1} (3.91 μ), which practically spells out a mercaptan group. In this case, the infrared spectrometer is at some disadvantage with respect to the nose. Had this been a thin film spectrum, we might have missed the S—H stretching band.

We now have the fragments: CH_2OH and SH. This only leaves a CH_2 group to fit in, and we write

$$HOCH_2CH_2SH$$

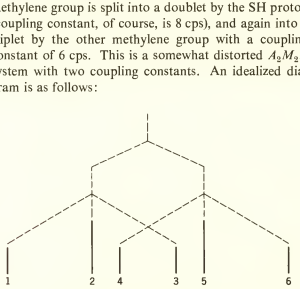
2-Mercaptoethanol

Some of the major fragmentation peaks can be assigned as follows:



The NMR spectrum provides exhaustive confirmation for the structure written. It also shows a number of interesting features. The starting point is the distribution of protons as shown by the integration curve. If we assume that the triplet at the high-field position contains one proton, then the next cluster of peaks contains two protons, and the low-field peaks account for three protons. At first glance, this does not seem reasonable. But we must bear several things in mind. First, the position of the OH peak and the SH peak depend on concentration. Since the OH-group forms stronger hydrogen-bonds than the SH-group, it is likely to be further downfield at a given concentration. Second, the OH proton will undergo rapid exchange under normal condition and will usually appear as a single peak; the SH proton, under the same conditions will not exchange rapidly (at least in a nonaqueous solvent), and the peak will be split by the adjacent methylene group.

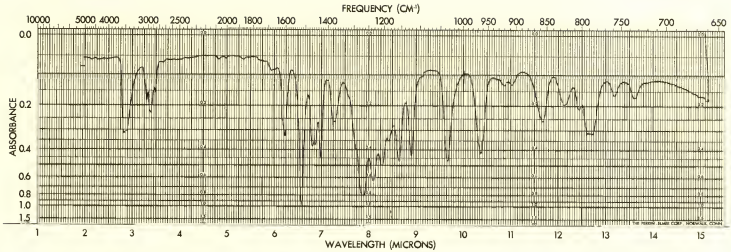
We see then that the upfield triplet (with slight second-order splitting of the middle peak) represents the SH proton coupled with (split by) the adjacent methylene group; the coupling constant is 8 cps. The adjacent methylene group is split into a doublet by the SH proton (coupling constant, of course, is 8 cps), and again into a triplet by the other methylene group with a coupling constant of 6 cps. This is a somewhat distorted A_2M_2X system with two coupling constants. An idealized diagram is as follows:



$$J_{12} = J_{23} = J_{45} = J_{56} = 6 \text{ cps}$$
$$J_{14} = J_{25} = J_{36} = 8 \text{ cps}$$

The low-field peaks must then consist of a triplet with a coupling constant of 6 cps, and it must also contain the OH-proton. We do indeed see a triplet with the upfield peaklet distorted by the peak of the OH proton with which it almost coincides. The hydroxyl proton peak can be shifted by change of concentration, solvent, or temperature.

Infrared Spectrum *Compound 6-8*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak	*m/e*	% of base peak
27	11.	66	5.	104	14.
29	6.	74	4.	105	8.
38	4.	75	4.	107	5.
39	17.	77	30.	121	16.
41	17.	78	8.	131	18.
43	5.	79	9.	132	6.
50	5.	80	4.	133	13.
51	12.	81	4.	137	8.
52	6.	89	5.	147	4.
53	10.	91	25.	149	30.
55	21.	92	5.	150	3.
62	6.	93	7.	163	5.
63	13.	94	7.	164	100.
64	5.	102	4.	165	11.10
65	14.	103	26.	166	1.04

ISOTOPE ABUNDANCES

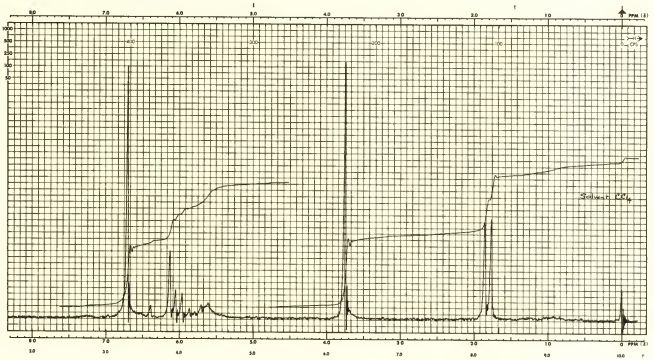
m/e	% of *P*
164 (*P*)	100.
165 (*P* + 1)	11.10
166 (*P* + 2)	1.04

Ultraviolet Data

	λ_{max}^{EtOH}	log ϵ_{max}
pH 7	263	4.2
	300 (*s*)	3.6
pH 13	288	4.0
	315 (*s*)	3.8

s = shoulder.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 8

The following empirical formulas fit the data for the parent peak and the $P + 1$ peak. We have eliminated trivial formulas and those containing an odd number of nitrogen atoms.

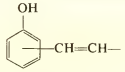
FORMULA	$P + 1$	$P + 2$
$C_8H_8N_2O_2$	9.61	0.81
$C_8H_{12}N_4$	10.36	0.49
$C_9H_8O_3$	9.97	1.05
$C_9H_{12}N_2O$	10.72	0.72
$C_{10}H_{12}O_2$	11.08	0.96
$C_{10}H_{16}N_2$	11.83	0.64

On the basis of the $P + 2$ peak, we can tentatively eliminate $C_8H_{12}N_4$ and $C_{10}H_{16}N_2$. The presence of an aromatic ring is indicated by the NMR peak at δ 6.70 τ 3.30 (distinctly upfield from the position of an unsubstituted benzene ring) and the general appearance of the infrared spectrum. We note a small peak at 3030 cm^{-1} (3.30 μ), strong peaks between 1600 and 1430 cm^{-1} (6.2 and 7.0 μ), and several moderately strong peaks in the low-frequency (long wavelength) region. As additional confirmation of aromaticity, we note that the parent peak in the mass spectrum is also the base peak.

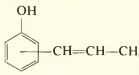
A conspicuous feature of the infrared spectrum is the rather strong absorption at 3510 cm^{-1} (2.85 μ). This is either an OH or an NH stretching band. We look to the region between 1230 and 1010 cm^{-1} (8.13 and 9.90 μ) for confirmation of OH absorption, but we are frustrated by the large number of bands in this region.

The U.V. spectrum gives us a good deal of information. The shift in wavelength at pH 13 is diagnostic for a phenol. Furthermore, the intense *K*-band at 263 mμ is indicative of a chromophore conjugated with the ring. In the absence of a carbonyl band in the infrared spectrum, we would suspect a C=C group. We quickly confirm this possibility by the olefinic proton absorption in the NMR spectrum at about δ 6.0, τ 4.0. A strong peak in the infrared spectrum at 965 cm^{-1} (10.36 μ) is evidence for *trans* olefinic hydrogens. The peak at 1605 cm^{-1} (6.23 μ) can probably be ascribed to the conjugated C=C stretching vibration.

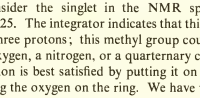
At this point we have the following information:



We now turn our attention to the doublet centered at δ 1.81, τ 8.19. The shift position is right for an allylic methyl group, and its existence as a doublet can be justified. Furthermore, we note the same spacing between several peaklets of the olefinic proton absorption as we note for the upfield doublet. We write



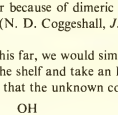
We consider the singlet in the NMR spectrum at δ 3.75, τ 6.25. The integrator indicates that this peak also contains three protons; this methyl group could be on a ring, an oxygen, a nitrogen, or a quarternary carbon. Its shift position is best satisfied by putting it on an oxygen and putting the oxygen on the ring. We have the following:



This adds up to 164 and to the empirical formula $C_{10}H_{12}O_2$. The benzene peak at δ 6.70, τ 3.30 contains three protons; the complex olefinic multiplet also accounts for three protons. Obviously, the phenolic proton is hidden under the olefinic multiplet.

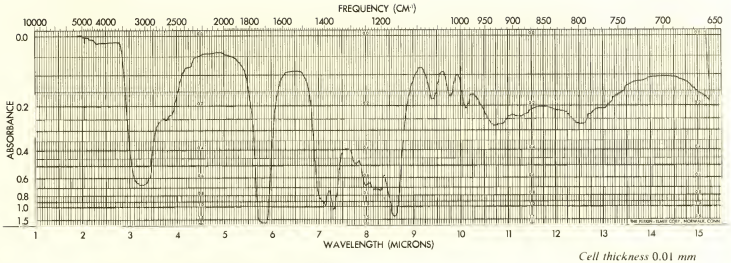
Assignment of the positions of the substituents is not easy. We cannot rely upon the C—H out-of-plane deformations in the long-wavelength region of the infrared spectrum because of the polar nature of the substituents. The NMR, which is usually very helpful for distinguishing among isomers, is of little use because the ring protons are all at the same shift value. We might note that the phenolic OH band in the infrared spectrum is at an unusually high frequency (short wavelength) considering that the spectrum was run neat. Partially hindered phenols (that is, a single ortho substituent) show this behavior because of dimeric rather than polymeric association (N. D. Coggeshall, *J. Am. Chem. Soc.* **72,** 2836 (1950)).

Having gotten this far, we would simply take a sample of isoeugenol off the shelf and take an IR spectrum. We would indeed find that the unknown compound is



isoeugenol

Infrared Spectrum *Compound 6-9*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	10.	45	12.
27	26.	55	33.
28	16.	56	33.
29	15.	57	4.
39	7.	73	8.
42	5.	98	13.
43	100.	99	3.
44	6.	116	2.44
		117	0.14
		118	0.03

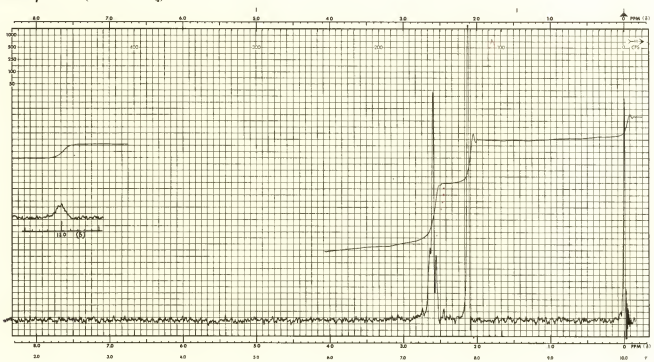
ISOTOPE ABUNDANCES

m/e	% of *P*
116 (*P*)	100.
117 (*P* + 1)	5.75
118 (*P* + 2)	1.4

Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
262	1.5

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 9

We list the empirical formulas under mass 116 that give a reasonable fit for the $P + 1$ value of 5.75%.

FORMULA	$P + 1$	$P + 2$
$C_3H_8N_4O$	4.94	0.30
$C_4H_8O_4$	4.54	0.88
$C_4H_8N_2O_2$	5.29	0.52
$C_4H_{12}N_4$	6.04	0.16
$C_5H_8O_3$	5.65	0.73
$C_5H_{12}N_2O$	6.40	0.37
$C_6H_{12}O_2$	6.75	0.59

The formulas which best fit our $P + 1$ value and our $P + 2$ value (1.4%) are $C_4H_8O_4$, $C_4H_8N_2O_2$, $C_5H_8O_3$, and $C_6H_{12}O_2$.

The infrared spectrum points to an aliphatic carboxylic acid. We note the very broad, bonded OH-stretching absorption extending between about 3330 and 2300 cm^{-1} (3.0 and 4.3 μ) with its characteristic pattern on its low-frequency (long wavelength) side. The strong C=O band at 1715 cm^{-1} (5.83 μ) satisfies the requirement for an aliphatic carboxylic acid. We find ready confirmation by noting the carboxylic acid proton at δ 11.0, τ – 1.0 in the NMR spectrum.

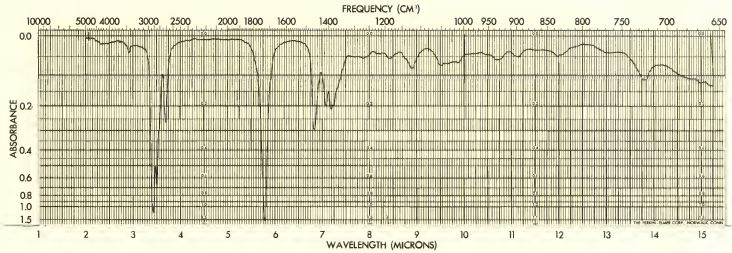
But the ultraviolet spectrum interposes a caveat. The low-intensity absorption at 262 mμ suggests an aliphatic unconjugated ketone. There is only one C=O band in the infrared spectrum, but it is rather broad; it must accommodate both the ketone and the acid C=O band. The fragmentation pattern does not resemble that of an ordinary aliphatic carboxylic acid; for one thing, there is no pronounced peak at mass 60. Since we are dealing with a ketone group in the molecule, we assume that the base peak of 43 in the mass spectrum arises from $CH_3C{=}O$. We now have the fragments $CH_3C{=}O$ and COOH which add up to mass 88. These leave us with an unknown mass of 28 for which we can write either C=O or CH_2—CH_2 or N_2.

The NMR spectrum allows us to make an unequivocal choice. The large singlet at δ 2.12, τ 7.88 must be the CH_3 group on the ketone carbonyl. If this peak contains three protons, then the distorted triplet at δ 2.60, τ 7.40 contains four protons. These must result from adjacent methylene groups which have almost the same chemical shift. We now write the structure

$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2COOH$$

levulinic acid

Infrared Spectrum — **Compound 6-10**



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	10.	55	55.
27	86.	56	7.
29	97.	57	50.
31	4.	58	5.
38	4.	67	7.
39	45.	68	14.
41	91.	69	5.
42	57.	70	73.
43	89.	71	23.
44	100.	72	7.
45	22.	81	14.
53	6.	85	3.
54	7.	86	12.
		96	6.
		113	0.2
		114	1.2
		115	0.13
		116	0.012

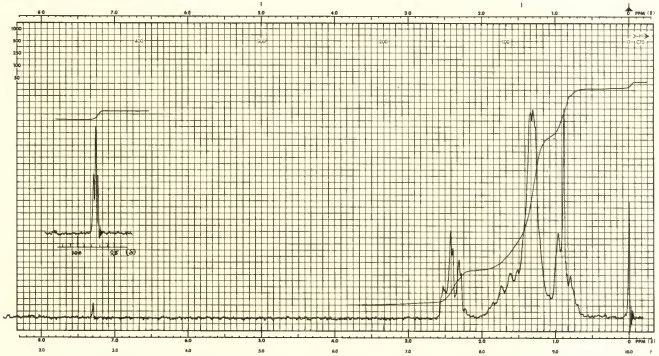
ISOTOPE ABUNDANCES

m/e	% of *P*
114 (*P*)	100.
115 (*P* + 1)	11.0
116 (*P* + 2)	0.97

Ultraviolet Data

$\lambda_{max}^{Cyclohexane}$	ϵ_{max}
292	23.2

NMR Spectrum *Solvent* $CDCl_3$)



COMPOUND NUMBER 10

In accordance with our usual procedure, we look at the empirical formulas under the parent mass (114) and try to select formulas that match our $P + 1$ and $P + 2$ peaks. But in this case, we find that our $P + 1$ peak is too high to match any of the formulas listed. The high value of the $P + 1$ peak can mean impurities. A more likely explanation is that this spectrum was obtained at a rather high inlet pressure in order to see the weak parent peak; we see a contribution to the $P + 1$ peak from a bimolecular addition of hydrogen to the parent ion. This is a common occurrence with molecules containing a hetero atom, which, as we shall see, is present. No sulfur or halogen is present.

The C=O band in the infrared spectrum at 1730 cm^{-1} (5.78 μ), together with the CH stretching band at 2703 cm^{-1} (3.70 μ), spells out an aldehyde group. This is readily confirmed by the characteristic ultraviolet spectrum, by the triplet in the NMR spectrum at δ 9.75, τ 0.25, and by the typical aldehyde base peak at mass 44. Furthermore, we know that we are dealing with an aliphatic primary aldehyde by the triplet structure of the aldehydic proton in the NMR (split by CH_2), by the weak parent peak and the mass 44 base peak in the mass spectrum, and by the lack of aromatic structure in either the NMR or the infrared spectra.

The absorption at δ 2.42, τ 7.58 in the NMR must represent the CH_2 next to the aldehyde group. It is split into a triplet by an adjacent CH_2 and again into a doublet by the aldehydic proton (small coupling constant). We now have

$$\underset{\text{mass 57}}{-CH_2CH_2CHO}$$

and we need a moiety of mass 57 to account for a molecular weight of 114. We could write

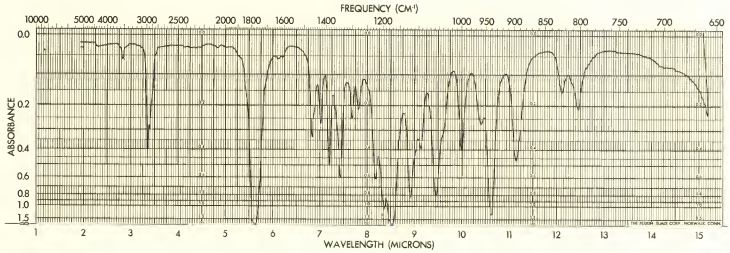
$$C_4H_9$$
$$C_3H_5O$$
$$C_2H_5N_2$$

The NMR integrator permits an unequivocal choice. If we assign one proton to the aldehydic absorption, and two protons to the adjacent methylene, there are eleven protons under the high-field absorption of which two belong to the β-methylene group. That leaves nine protons for the missing moiety which is obviously C_4H_9. Furthermore, we can make out a distorted triplet centered on δ 0.89, τ 9.11 which represents a CH_3 group. The ratio of the area of this triplet to the area of the absorption of the methylene groups between δ 2.0, τ 8.0, and δ 1.1, τ 8.9 is 3:8. Therefore, the chain is not branched. The compound is

$$\underset{\text{Heptaldehyde}}{CH_3CH_2CH_2CH_2CH_2CH_2CHO}$$

The peaks in the mass spectrum at mass 96 ($P - H_2O$), mass 86 ($P - CO$), and at mass 70 ($P - CH_2CH_2OH$) confirm the choice of mass 114 as the parent peak despite its low intensity.

Infrared Spectrum *Compound 6-11*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	22.	44	4.
27	48.	45	6.
29	72.	55	11.
30	4.	56	100.
38	4.	57	12.
39	19.	85	47.
41	58.	100	4.2
42	10.	101	0.28
43	37.	102	0.034

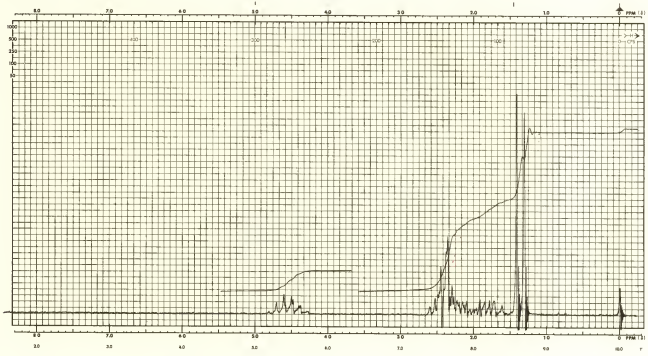
ISOTOPE ABUNDANCES

m/e	% of *P*
100 (*P*)	100.
101 (*P* + 1)	6.63
102 (*P* + 2)	0.8

Ultraviolet Data

Transparent above 200 mμ

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 11

The likely empirical formulas under mass 100 on the basis of our $P + 1$ peak (6.63%) are

FORMULA	$P + 1$	$P + 2$
$C_4H_8N_2O$	5.25	0.31
$C_5H_8O_2$	5.61	0.53
$C_5H_{12}N_2$	6.36	0.17
$C_6H_{12}O$	6.72	0.39

Our $P + 2$ peak (0.8%) would tend to favor $C_5H_8O_2$, but $C_6H_{12}O$ is a possibility because of its close agreement with the $P + 1$ peak.

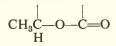
The strong C=O band at 1780 cm^{-1} (5.62 μ) in the infrared, together with the strong broad absorption band at 1170^{-1} (8.55 μ), suggests an ester, but the C=O band is at a rather high frequency (short wavelength) for an ordinary ester. Halogen substituents would account for this, but, obviously, chlorine or bromine are absent. Even more obviously, iodine is not present, but fluorine must still be kept in mind, although there are no suspicious peaks in the mass spectrum.

There is moderate absorption in the infrared spectrum in the low-frequency (long wavelength) end of the spectrum, but none between 1667 and 1471 cm^{-1} (6.0 and 6.8 μ); nor is there anything to suggest aromatic CH stretching vibration. On balance, we do not seem to be dealing with an aromatic compound. This impression is reinforced by the ultraviolet and the NMR spectra.

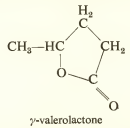
Since two oxygen atoms are probably present, we adopt $C_5H_8O_2$ as the empirical formula, (forgetting about fluorine for the moment). The formula suggests unsaturation, but none of the spectra bear out this possibility.

There are two conspicuous features in the NMR spectrum. We note the low-field quartet (with further splitting) and the high-field doublet in the ratio 1:3; we note that they are coupled, and we write $CH_3—CH$. This, together with the —O—C=O group, adds up to a mass of 72. Subtraction from the molecular weight leaves a mass of 28, which we can account for as $—CH_2—CH_2—$; we dismiss the possibility of a fluorine atom.

The CH is at a very low-field position which can be accounted for nicely if we write



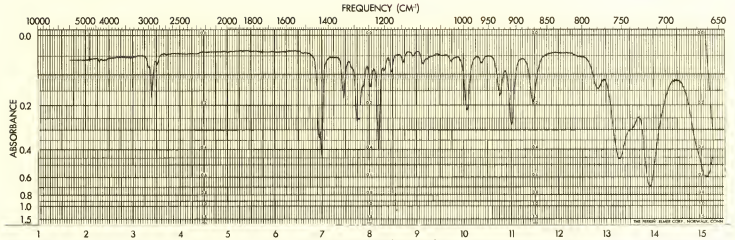
Now if we simply bridge the gap with the two methylene groups, we wind up with the compound



γ-valerolactone

All the pieces fall into place. The (apparently) anomalous position of the carbonyl absorption in the infrared is explained. We might have arrived at the answer sooner had we recognized the characteristic position of the C=O band of a five-membered ring lactone. The C-to-H ratio is justified, and the unfamiliar mass 56 base peak in the mass spectrum must result from elimination of —O—C=O from the ring.

Infrared Spectrum **Compound 6-12**



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	8.	64	4.
27	14.	75	100.
35	5.	76	4.
36	4.	77	32.
37	8.	83	3.
38	9.	96	3.
39	28.	97	19.
40	3.	98	3.
41	6.	99	11.
42	3.	110	32.
49	20.	111	3.
50	3.	112	21.
51	13.	114	4.
55	3.	146	0.12
61	32.	148	0.11
62	14.	150	0.04
63	11.	152	trace

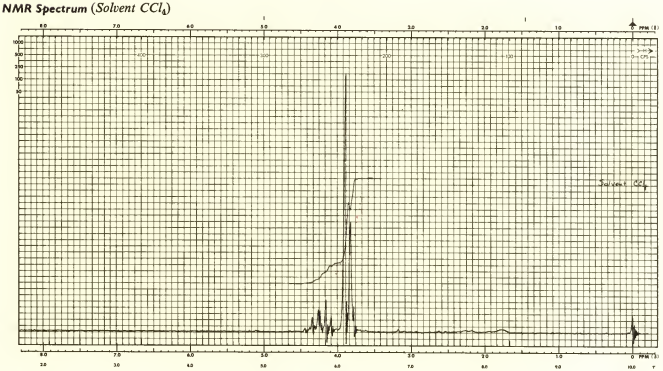
ISOTOPE ABUNDANCES

m/e	% of *P*
146 (*P*)	100.
148 (*P* + 2)	93.
150 (*P* + 4)	30.
152 (*P* + 6)	...

Ultraviolet Data

λ_{max}^{EtOH}	ϵ_{max}
242	14.5

NMR Spectrum (*Solvent* CCl_4)

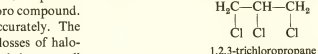


COMPOUND NUMBER 12

A casual glance at the mass spectrum tells us that we are concerned with a polychloro, a polybromo, or a mixed chlorobromo compound. From Table II in Chapter 2, we ascertain that the P, $P+2$, and $P+4$ pattern closely resembles that calculated for a trichloro compound. The $P+6$ peak is too small to measure accurately. The fragmentation pattern shows consecutive losses of halogen-containing fragments. The parent peak is so small that the $P+1$ peak is hardly noticeable, but this fact should be of little consequence. If we subtract the mass of three chlorine atoms from 146, we are left with a mass of 41 to account for. This could be

C_3H_5
or
C_2HO
or
CHN_2

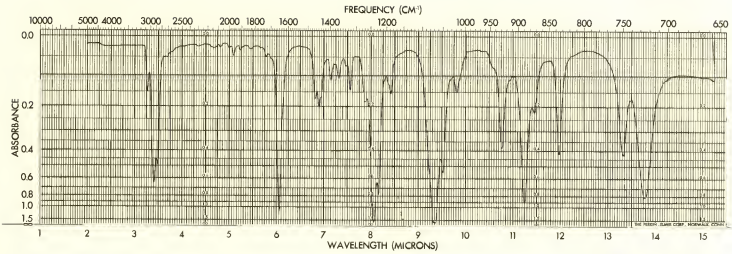
The infrared spectrum eliminates carbonyl or ether groups from consideration. The strong absorption bands between about 750 and 650 cm^{-1} (13.3 and 15.4 μ) are the C—Cl stretching bands and not aromatic absorption. The remainder of the spectrum is in accord with an aliphatic structure. Certainly C_3H_5 looks like the most valid of the possibilities. The only question left is how to distribute the three chlorine atoms on the three carbon atoms. The NMR spectrum shows two discrete absorption areas in the ratio of 1:4. This in itself leads us to write



1,2,3-trichloropropane

This compound should represent an A_4B system, and we do recognize a distorted doublet. The quintuplet is badly distorted. These distortions are a function of a small $\delta_2 - \delta_1/J$ value.

Infrared Spectrum *Compound 6-13*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	20.	53	14.
27	61.	54	23.
37	3.	55	100.
38	5.	56	28.
39	33.	57	10.
41	23.	69	9.
42	5.	83	24.
43	6.	84	50.0
50	7.	85	2.83
51	7.	86	0.23

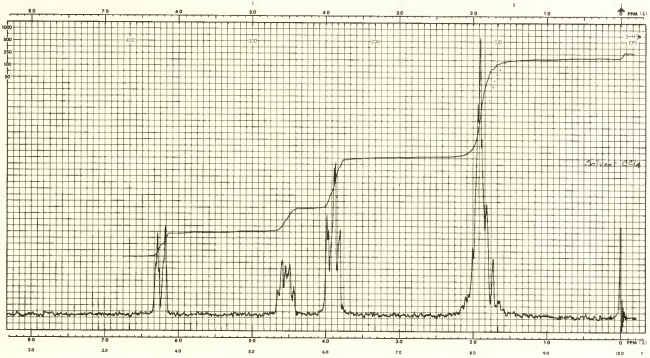
ISOTOPE ABUNDANCES

m/e	% of *P*
84 (*P*)	100.
85 (*P* + 1)	5.65
86 (*P* + 2)	0.45

Ultraviolet Data

Transparent in near ultraviolet.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 13

The possible empirical formulas for a molecular weight of 84 are

FORMULAS	$P+1$	$P+2$
$C_4H_4O_2$	4.47	0.48
$C_4H_8N_2$	5.21	0.11
C_5H_8O	5.57	0.33
C_6H_{12}	6.67	0.19

The best match for the $P+1$ peak (5.65%) and for the $P+2$ peak (0.45%) is C_5H_8O.

The general impression given by the infrared spectrum is that we are dealing with an aromatic carbonyl compound. But discrepancies rapidly become apparent. For one thing, the ultraviolet spectrum effectively rules out aromatic or heteroaromatic ring systems; there is no evidence for a ketone or aldehyde group. The empirical formula rules out esters and amides. A closer look at the infrared spectrum reveals a disturbing ratio of the intensities of the aliphatic CH stretching absorption at 2933 cm^{-1} (3.41 μ) and the "carbonyl" band at 1650 cm^{-1} (6.06 μ). The empirical formula does not permit a heavily alkylated ring system.

The NMR spectrum shows a doublet (with additional splitting) at δ 6.21, τ 3.79. This is at the high-field end for aromatic and heteroaromatic protons, and at the low-field end for olefinic protons. If we assume that we are dealing with an olefin, the spectra all make more sense. The "carbonyl" band in the infrared now becomes an intensified C=C stretching band. The small peak at 3058 cm^{-1} (3.27 μ) is obviously the olefinic CH stretching band, and the long wavelength absorption must be a somewhat displaced strong cisoid bending band.

If we assign one olefinic proton to the downfield absorption in the NMR spectrum, we can then tentatively assign another olefinic proton to the multiplet at δ 4.55, τ 5.45. We can detect the same spacing ($J = 7$ cps) in both sets of peaks; this coupling constant is of the proper magnitude for *cis* olefinic protons.

In order to explain the extreme downfield position of one olefinic CH, we will place the oxygen atom, allowed by the empirical formula, adjacent to this CH. We can now write —O—CH=CH—. The intense band at 1241 cm^{-1} (8.06 μ) in the infrared spectrum will support a vinyl ether structure.

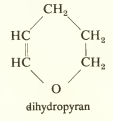
We now subtract the vinyl ether moiety from the empirical formula

$$\begin{array}{r} C_5H_8O \\ C_2H_2O \\ \hline C_3H_6 \end{array}$$

Further consideration of the NMR spectrum allows us to make a rational distribution of the C and H atoms. The six protons are distributed under two peaks in the ratio of 2:4. The smaller peak, an apparent triplet with additional splitting, is moved strongly downfield; we are justified in putting it on the oxygen atom

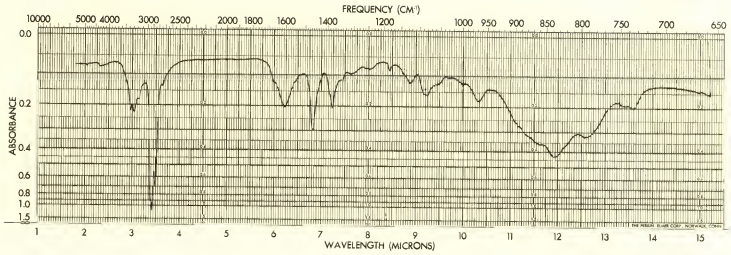
$$—H_2C—O—CH=CH—.$$

We can now close the gap with $—CH_2—CH_2—$ and write



dihydropyran

Infrared Spectrum *Compound 6-14*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak
27	8.
29	4.
30	100.
39	4.
41	4.
73	5.44
74	0.30
75	0.011

ISOTOPE ABUNDANCES

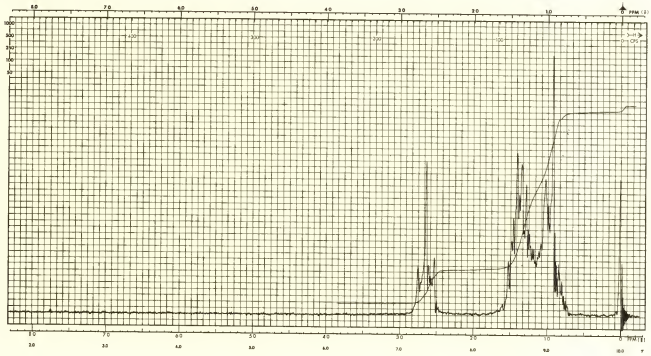
m/e	% of *P*
73 (*P*)	100.
74 (*P* + 1)	5.5
75 (*P* + 2)	0.2

Ultraviolet Data

λ_{max}^{EtOH}	ϵ_{max}
225 (*s*)	56

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 14

The parent mass is an odd number. We therefore select empirical formulas under mass 73 that contain an odd number of nitrogen atoms.

FORMULA	$P+1$	$P+2$
C_3H_7NO	3.77	0.25
$C_4H_{11}N$	4.88	0.10

The base peak, mass 30, is diagnostic for an aliphatic amine. The two peaks in the infrared spectrum at 3367 cm^{-1} (2.97 μ) and at 3279 cm^{-1} (3.05 μ) are indicative of a primary amine; this would have been more convincing in dilute solution. There is no evidence for aromaticity or for olefinic bonds. The broad absorption with the maximum at about 840 cm^{-1} (11.9 μ) in the infrared spectrum, results from NH bending vibrations, as does the medium absorption at 1603 cm^{-1} (6.24 μ).

We note the triplet in the NMR spectrum at δ 2.64, τ 7.36, which must be the CH_2 group next to the NH_2. Because of its splitting, we know it is also adjacent to another CH_2 group. We can write $—CH_2—CH_2—NH_2$. The ratio of the area of the low-field triplet to that of the complex upfield absorption is 2 : 9. The NH_2 protons are buried in the upfield absorption; it is probably the peak at δ 1.02, τ 8.98. This could be checked by either heating or diluting the solution.

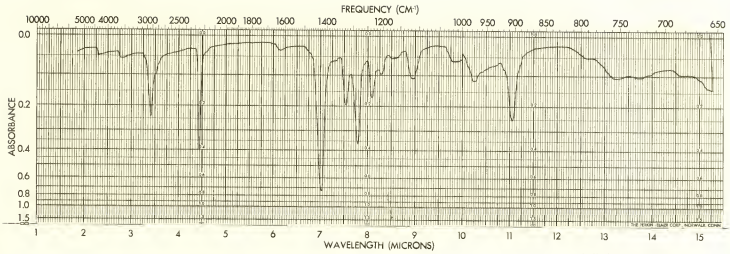
Since the empirical formula $C_4H_{11}N$ permits only C_2H_5 in addition to the fragment shown above, the compound is

$$CH_3—CH_2—CH_2—CH_2—NH_2$$

n-butylamine

The intense sharp peak at δ 0.91, τ 9.09 is the middle peak of the distorted CH_3 triplet.

Infrared Spectrum *Compound 6-15*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	86.	51	28.
27	48.	52	66.
28	28.	53	66.
32	8.	54	100.
33	8.	55	6.
34	11.	57	6.
37	5.	58	8.
38	9.	59	17.
39	6.	60	8.
40	6.	73	5.
41	15.	87	20.
42	8.	100	44.
45	25.	113	3.
46	16.	140	14.8
47	57.	141	1.40
50	6.	142	0.85

ISOTOPE ABUNDANCES

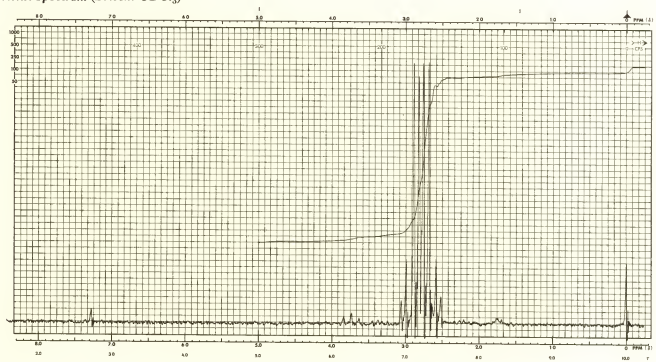
m/e	% of *P*
140 (*P*)	100.
141 (*P* + 1)	9.54
142 (*P* + 2)	5.77

Ultraviolet Data

λ_{max}^{EtOH}	ϵ_{max}
222 (*s*)	100

(*s*) = shoulder.

NMR Spectrum (*Solvent* $CDCl_3$)



COMPOUND NUMBER 15

The molecular weight is 140, and the compound obviously contains one atom of sulfur. We look under mass 108, allowing for a 0.78 contribution to the $P + 1$ peak. We write the empirical formulas starting arbitrarily with $P + 1 = 6.27$ and eliminating formulas containing an odd number of nitrogen atoms:

FORMULA	$P + 1$
$C_5H_4N_2O$	6.27
$C_6H_4O_2$	6.63
$C_6H_8N_2$	7.38
C_7H_8O	7.73
C_8H_{12}	8.84

The infrared spectrum conveys an aliphatic impression; nor is there any indication of unsaturation or aromaticity in the ultraviolet or NMR spectrum. The sharp band at 2247 cm^{-1} (4.45 μ) in the infrared stands out conspicuously. There are only a few possibilities: An isocyanate or a nitrile are the most probable candidates.

Thus far, we can account for a sulfur atom, presumably as a sulfide, and for a nitrogen atom. In order to account for the even mass, we need another nitrogen atom which could be another isocyanate or nitrile group or possibly a tertiary amine. The correct empirical formula must be either $C_5H_4N_2O$ or $C_6H_8N_2$. Neither empirical formula will accommodate two isocyanate groups.

Let us consider the fragmentation pattern. The base peak is mass 54 which is just half of the nonsulfur-containing moiety. We seem to be dealing with a symmetrical molecule, and a glance at the NMR spectrum confirms this. We think in terms of a symmetrical dinitrile. Confirmational details now become apparent. The next largest peak in the fragmentation pattern is mass 26, obviously the C≡N group from each end. The mass 41 peak (CH_2—C≡N + H), which we look for in aliphatic nitriles, is prominent. The mass 100 peak is large, and this may result from loss of a $CH_2C{\equiv}N$ fragment. There appear to be a number of rearrangement peaks; this is reasonable in a molecule containing three hetero atoms.

The base peak of mass 54 must represent

$$CH_2—CH_2—C{\equiv}N$$

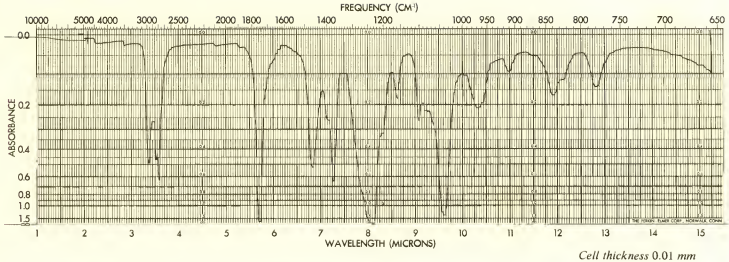
and the complete molecule must be

$$N{\equiv}C—CH_2—CH_2—S—CH_2—CH_2—C{\equiv}N$$

β,β'-thiodipropionitrile

The NMR spectrum is an example of an A_2B_2 coupling with a small $\delta_2 - \delta_1/J$ value.

Infrared Spectrum *Compound 6-16*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	3.	55	3.
27	6.	56	7.
28	9.	57	3.
30	6.	58	100.
41	4.	59	4.
42	23.	71	11.
43	17.	131 (*P*)	0.346
44	7.		

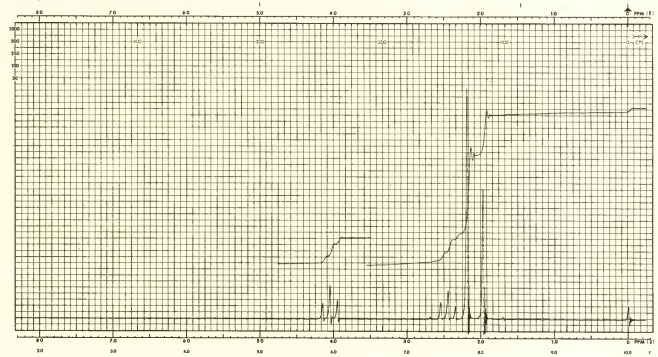
ISOTOPE ABUNDANCES

$P + 1$) Too small
$P + 2$) to measure

Ultraviolet Data

Transparent above 210 mμ.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 16

The parent ion peak (mass 131) of this compound was very small. The $P + 1$ and $P + 2$ peaks were too small for accurate measurement of intensity, and we cannot arrive at an empirical formula.

The molecular weight calls for an odd number of nitrogen atoms; let us begin with a single nitrogen atom. In the absence of evidence for primary or secondary amines, nitriles, amides, nitro compounds, or heteroaromatic compounds, we shall assume we may be dealing with a tertiary amine. There is no evidence for unsaturation or aromaticity in any of the spectra.

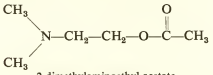
The infrared spectrum shows a strong carbonyl band at 1748 cm^{-1} (5.72 μ) and a typical broad strong C—O—C band at about 1235 cm^{-1} (8.10 μ). This combination is evidence for the presence of an acetate group. As supporting evidence there is a prominent mass 43 ($CH_3C{=}O$) in the infrared spectrum, and a singlet at δ 1.95, τ 8.05 in the NMR spectrum, which we may attribute to the CH_3 of the acetate group.

The NMR spectrum shows two triplets of equal areas with the same spacings. We are justified in writing $-CH_2-CH_2-$ and in placing the more deshielded methylene group on the oxygen of the acetate group;

thus, $-CH_2-CH_2-O-C-CH_3$.

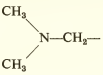
We have postulated the presence of a tertiary amine group. The molecular weight allows for C_2H_6N. The singlet at δ 2.20, τ 7.80 in the NMR, with double the area of the acetate CH_3 group, permits us to write

We can now write the complete structure

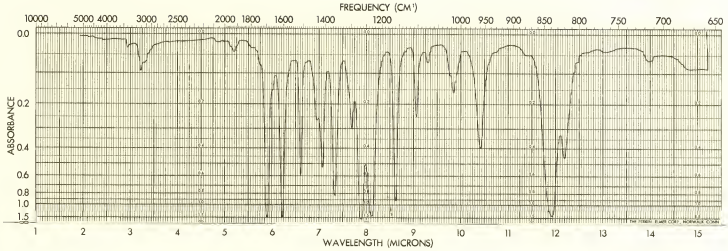


2-dimethylaminoethyl acetate

There are other possible lines of observation and reasoning we could have followed. The base peak, mass 58, is a characteristic amine fragmentation peak which results from cleavage of the bond beta to the nitrogen atom. This, together with consideration of the other spectra, would have lead us directly to the fragment



Infrared Spectrum *Compound 6-17*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
39	3.	74	5.
43	17.	75	20.
50	9.	123	100.
51	5.	124	8.
57	4.	138	20.0
68	3.	139	2.04
69	5.	140	0.114

ISOTOPE ABUNDANCES

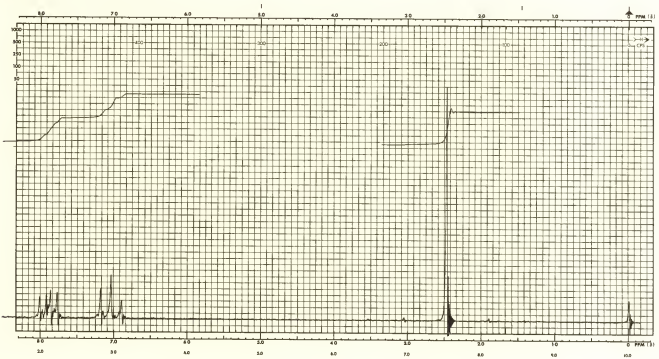
m/e	% of *P*
138 (*P*)	100.
139 (*P* + 1)	10.2
140 (*P* + 2)	0.57

Ultraviolet Data

$\lambda_{max}^{Isooctane}$	ϵ_{max}
240	16,900
268	762
275	466
278(*s*)	258
292(*s*)	86
312	71

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 17

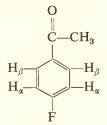
As usual, we list the likely empirical formulas:

FORMULA	$P+1$	$P+2$
$C_8H_{10}O_2$	8.88	0.75
$C_8H_{14}N_2$	9.63	0.42
$C_9H_{14}O$	9.99	0.65

The infrared spectrum shows a strong C=O band at 1695 cm^{-1} (5.90 μ). We suspect some form of conjugation from its position. The strong band at 838 cm^{-1} (11.93 μ) leads us to think tentatively in terms of a 1,4-disubstituted benzene ring. The weak band at 3096 cm^{-1} (3.23 μ) offers further support for the presence of an aromatic ring. There is strong absorption in the region near 1250 cm^{-1} (8.0 μ) which may be an ester C—O—C band. However, the strong *K*-band in the ultraviolet spectrum at 240 mμ, the benzenoid fine structure, and the weak *R*-band at 312 mμ offer convincing evidence for a ketone carbonyl conjugated with a ring.

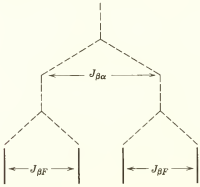
If we are on the right track, the base peak of the mass spectrum should represent this structure. The mass of the ring substituent can then be obtained by subtracting mass 104 ($C_6H_4C{=}O$) from the base peak (123); we must therefore account for a substituent of mass 19. The very strong possibility of a fluorine atom must be entertained, and our empirical formulas may not be valid. The position in the infrared spectrum of a C—F stretching vibration is in the region of 1111–1000 cm^{-1} (9.0–10.0 μ), and we do see a band of moderate intensity at 1104 cm^{-1} (9.06 μ).

We noted that the benzene ring is probably 1,4-disubstituted. We write the structure



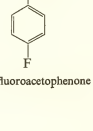
and we look to the NMR spectrum for verification. We note two low-field multiplets and a high-field singlet; the areas are respectively 2 : 2 : 3. The high-field singlet obviously represents the CH_3 protons of the acetyl group. The multiplet at lowest field represents the H_β protons, and the multiplet centered at α 7.05, τ 2.95 represents the H_α protons. We can justify the assignments on the basis of the coupling constants $J_{\alpha\beta}$, $J_{\alpha F}$, and $J_{\beta F}$; we ignore the very small para coupling constants of the protons. We recall that the fluorine atom couples with protons and, by reference to Appendix D of Chapter 4, we see that H—F couplings in a benzene ring are of the same order of magnitude as H—H couplings.

Consider first the H_β protons. They are coupled to the H_α-protons ($J_{\beta\alpha}$ = 8 cps) and to the F atom ($J_{\beta F}$ = 5 cps). This coupling results in two pairs of peaks.



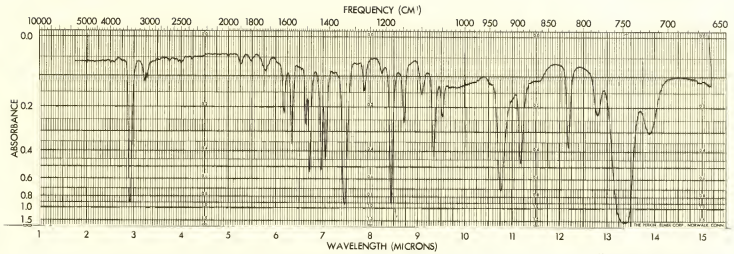
The H_α-protons are coupled to the H_β-protons ($J_{\alpha\beta}$ = 8 cps) and to the F atom ($J_{\beta F}$ = 8 cps). Since the couplings are identical, the result is a triplet.

The compound is



p-fluoroacetophenone

Infrared Spectrum — **Compound 6-18**



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	3.	88	5.
37	4.	89	29.
38	4.	90	4.
39	7.	114	3.
41	3.	115	6.
50	4.	116	18.
57½	6.	123	6.
61	5.	124	11.
62	10.	125	3.
63	12.	126	4.
73	3.	150	5.
75½	11.	151	100.
76½	4.	152	10.4
86	3.	153	32.1
87	5.	154	2.89

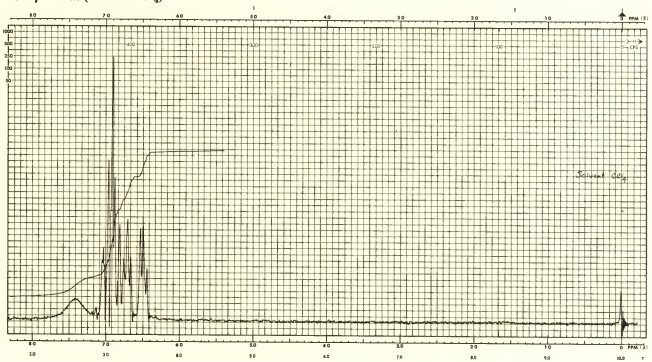
ISOTOPE ABUNDANCES

m/e	% of *P*
151 (*P*)	100.
152 (*P* + 1)	10.4
153 (*P* + 2)	32.1
154 (*P* + 3)	2.89

Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
218	4.61
272	3.88
278	3.89
288	3.77

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 18

The $P + 2$ peak (32.1%) allows for the presence of a single chlorine atom. We subtract mass 35 from the parent mass and obtain mass 116 for the rest of the molecule. The best fit to our $P + 1$ peak is afforded by the following empirical formulas:

FORMULA	$P + 1$
$C_7H_4N_2$	8.39
$C_7H_{16}O$	7.86
C_8H_4O	8.75
C_8H_6N	9.12
C_9H_8	9.85

Since the parent mass is an odd number, the molecule contains an odd number of nitrogen atoms. Since the parent peak is also the base peak, the compound is aromatic. The only one of our formulas that fits is C_8H_6N.

Supporting evidence for a high degree of aromaticity is found in all of the spectra. The CH stretching region of the infrared, in fact, shows only aromatic C—H absorption. There are five strong bands between 1667 and 1429 cm^{-1} (6.0 and 7.0 μ) and four strong bands between 1000 and 715 cm^{-1} (10.0 and 14.0 μ). The strong sharp band at 3413 cm^{-1} (2.93 μ) is an invitation to place a hydrogen atom on the nitrogen atom we know to be present.

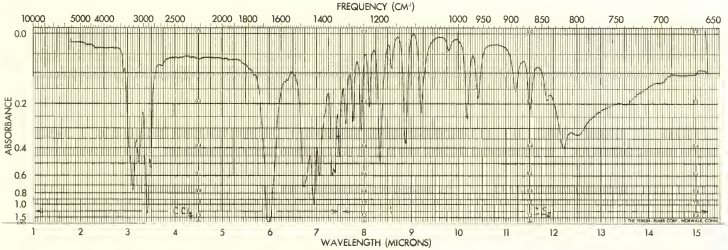
We are obviously not dealing with an aliphatic amine. Nor does an aromatic amine or a pyridine type molecule fit the picture; in the former case, we would have noted decreased ultraviolet absorption at pH 1, and in the latter case, enhanced absorption. No change in the ultraviolet spectrum is reported.

The NMR spectrum shows a broad, flat absorption centered at δ 7.40, τ 2.60. This is a typical NH absorption. Its downfield position, together with the failure mentioned above to respond to change in pH is strongly suggestive of a pyrrole or an indole NH.

With this information, we would write a chloroindole structure with the Cl atom on the benzene ring. The protons on the pyrrole ring are visible as triplets centering at δ 6.71, τ 3.29 for the 2-H, and at δ 6.50, τ 3.50 for the 3-H. Apparently the protons are not only coupled to each other, but each is also coupled to the proton on nitrogen. It is not possible from the available data to assign the position of Cl substitution because a Cl atom has very little effect on the position of ring protons. Reference spectra are needed to tell us that the compound is

4-chloroindole

Infrared Spectrum *Compound 6-19*



Cell thickness 0.09 *mm*
(10% *Solution*)

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	10.	54	4.
27	42.	55	81.
24	21.	56	50.
30	100.	57	9.
31	3.	67	6.
38	4.	68	4.
39	30.	83	5.
41	48.	84	32.
42	53.	85	28.
43	16.	113	45.0
44	7.	114	3.0
53	4.	115	0.21

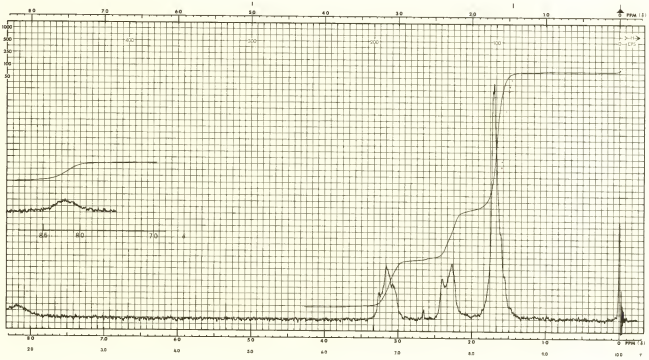
ISOTOPE ABUNDANCES

m/e	% of *P*
113 (*P*)	100.
114 (*P* + 1)	7.10
115 (*P* + 2)	0.46

Ultraviolet Data

*Et*OH–Featureless
210–240 mμ

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 19

Under mass 113, we select the following empirical formulas which contain an odd number of nitrogen atoms:

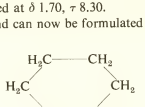
FORMULA	$P+1$	$P+2$
$C_5H_7NO_2$	5.98	0.55
$C_8H_{11}N_3$	6.72	0.19
$C_6H_{11}NO$	7.08	0.42
$C_7H_{15}N$	8.19	0.29

The best fit is $C_6H_{11}NO$. The strong carbonyl band at 1669 cm^{-1} (5.99 μ), in the infrared spectrum, together with the series of bands in the region between 3448 and 3077 cm^{-1} (2.90 and 3.25 μ) suggests an amide group, but the absence of an amide II band makes a lactam seem more likely. The ultraviolet and the NMR spectra rule out aromatic structure and olefinic protons, although very broad absorption in the long wavelength region of the infrared spectrum may have raised the question of aromaticity. This long wavelength absorption is probably the out-of-plane NH bending vibration.

The molecular weight permits us to write a six-carbon lactam structure. All that remains is to determine the size of the ring and positions of substituents. We can ascribe the broad flat absorption centered at about δ 8.2, τ 1.8 in the NMR spectrum to a hydrogen on a lactam nitrogen. We have the following fragment:

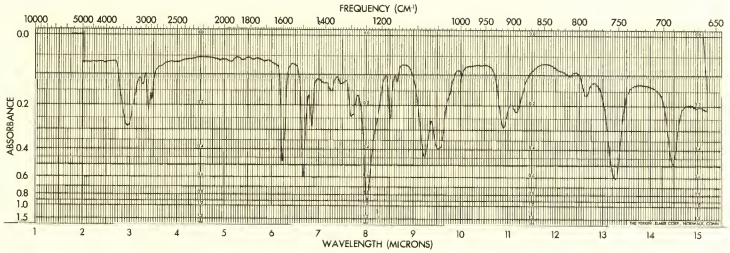
The broad apparent triplet at δ 3.2, τ 6.8 in the NMR spectrum must represent a CH_2 group on the N atom, and a somewhat less deshielded CH_2 group on the C=O group would account for the absorption at about δ 2.3, τ 7.7. The integrator tells us that there are six protons under the peak centered at δ 1.70, τ 8.30.

The compound can now be formulated as



ε-caprolactam

Infrared Spectrum *Compound 6-20*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
29	7.	66	16.
31	7.	77	34.
38	4.	78	4.
39	15.	79	5.
40	3.	94	100.
43	4.	95	13.
45	11.	107	8.
51	13.	138	26.7
63	6.	139	2.40
64	3.	140	0.22
65	15.		

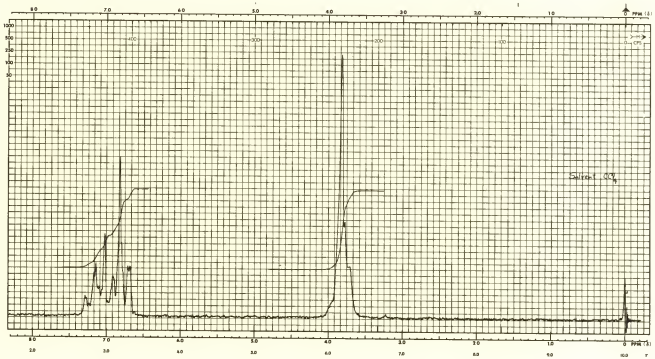
ISOTOPE ABUNDANCES

m/e	% of *P*
138 (*P*)	100.
139 (*P* + 1)	8.99
140 (*P* + 2)	0.82

Ultraviolet Data

$\lambda^{\text{Isooctane}}_{\text{max}}$	log ϵ_{max}
219	3.96
253	3.22
260	3.36
267	3.35

NMR Spectrum (*Solvent* CCl_4)



COMPOUND NUMBER 20

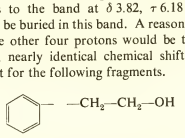
Under molecular weight 138, we list the following empirical formulas:

FORMULA	$P+1$	$P+2$
$C_6H_6N_2O_2$	7.42	0.64
$C_6H_{10}N_4$	8.17	0.30
$C_7H_6O_3$	7.78	0.86
$C_7H_{10}N_2O$	8.53	0.52
$C_8H_{10}O_2$	8.88	0.75
$C_8H_{14}N_2$	9.63	0.42

The strong absorption bands at 754 cm^{-1} (13.26 μ) and 690 cm^{-1} (14.49 μ), together with the weak C—H stretching band at 3058 cm^{-1} (3.27 μ) and absorption between 1613 and 1471 cm^{-1} (6.2 and 6.8 μ), suggest a monosubstituted benzene ring. The moderately strong, fairly broad band at 3390 cm^{-1} (2.95 μ) looks more like an OH-band than an NH-band. The OH bending region has three bands, and we cannot, at this point, tell whether we are dealing with a phenol, a primary alcohol, or a secondary alcohol. The ultraviolet spectrum shows only benzenoid absorption and a band at 219 mμ which could be a weak *K*-band, but which is more likely an *E*-band. A phenol is no longer considered because no change at pH 13 is reported in the ultraviolet spectrum.

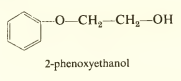
The base peak in the mass spectrum is 94. This, being an even number, must result from two cleavages or from a rearrangement. It does not help us much at this point. We note, in passing, the benzene ring masses at 77, 78, and 79. We look at mass 31 and mass 45 for indications of a primary or secondary alcohol. Both mass 31 and mass 45 are present but are rather small.

The NMR spectrum shows the ring proton absorption at about δ 7.3, τ 2.7 to about δ 6.6, τ 3.4. If we assign five-ring protons to this absorption, we must also assign five protons to the band at δ 3.82, τ 6.18; the OH-proton must be buried in this band. A reasonable assignment for the other four protons would be to two CH_2 groups with nearly identical chemical shifts. We can now account for the following fragments.



The total mass of these fragments is 122. The molecular weight (138) permits the inclusion of an oxygen. Our empirical formula is thus $C_8H_{10}O_2$, in agreement with the formula that best matches the isotope abundance data.

It is not difficult to arrange the fragments. We probably should have looked harder at the strongest peak in the infrared spectrum at 1245 cm^{-1} (8.03 μ). Now that we think in terms of a phenyl alkyl ether, this band provides welcome confirmation. The base peak in the mass spectrum then must result from the characteristic cleavage and hydrogen rearrangement of this type of ether. The base fragment is C_6H_5OH, and the total structure must be



2-phenoxyethanol

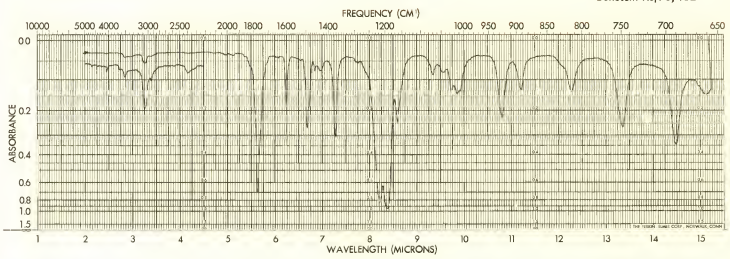
CHAPTER SEVEN

Sets of Spectra with Beilstein References

This chapter consists of ten sets of spectra. Each compound represented by a set of spectra is identified by a reference to Beilstein. We again remind the reader that the compounds contain only C, H, O, N, S, and the halogens.

Infrared Spectrum

Compound No. 7-I
Beilstein Ref. 6, 152



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
28	5.	63	4.
38	5.	65	11.
39	18.	66	12.
40	3.	94	100.
42	3.	95	7.
43	29.	136	10.1
50	3.	137	0.885
51	4.	138	0.076

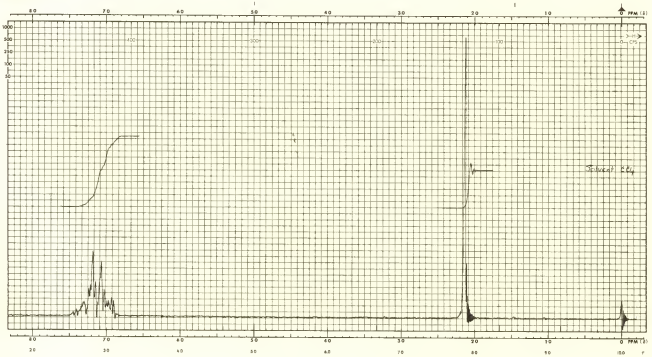
ISOTOPE ABUNDANCES

m/e	% of *P*
136 (*P*)	100.
137 (*P* + 1)	8.77
138 (*P* + 2)	0.74

Ultraviolet Data

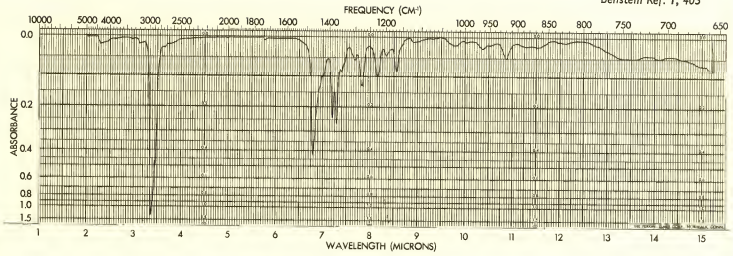
λ_{max}^{EtOH}	log ϵ_{max}
248	2.02
253	2.15
259	2.24
265	2.12

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound No. 7-2
Beilstein Ref. 1, 405



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	20.	55	34.
28	3.	56	3.
29	16.	57	3.
39	11.	61	37.
41	28.	69	9.
42	12.	70	100.
43	37.	71	16.
45	6.	103	15.
46	5.	131	5.
47	7.	174	17.3
		175	2.09
		176	0.91

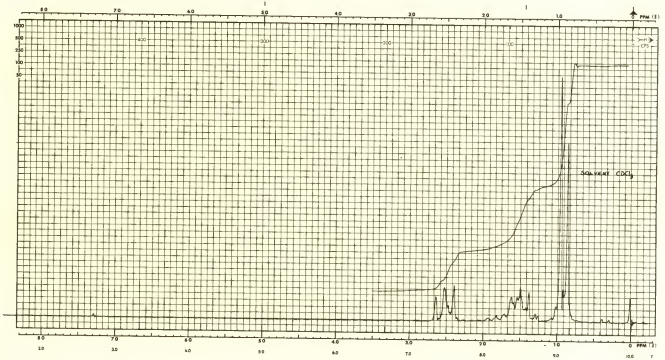
ISOTOPE ABUNDANCES

m/e	% of *P*
174 (*P*)	100.
175 (*P* + 1)	12.1
176 (*P* + 2)	5.25

Ultraviolet Data

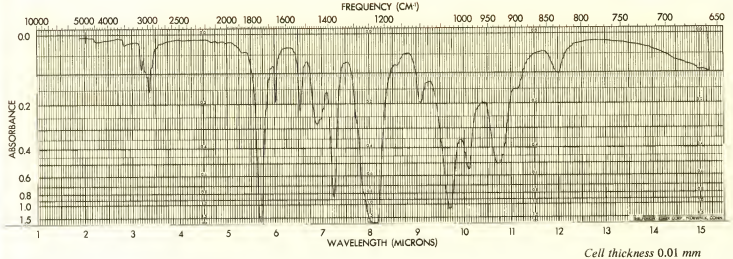
Featureless above 210 mμ.

NMR Spectrum (*Solvent* $CDCl_3$)



Infrared Spectrum

Compound No. 7-3
Beilstein Ref. **2,** *136*



Cell thickness 0.01 *mm*

Mass Spectral Data
(Relative Intensities)

m/e	% of base peak
26	4.
27	8.
29	7.
38	3.
39	16.
41	16.
42	4.
43	100.
57	7.
58	9.
100	0.1

ISOTOPE ABUNDANCES

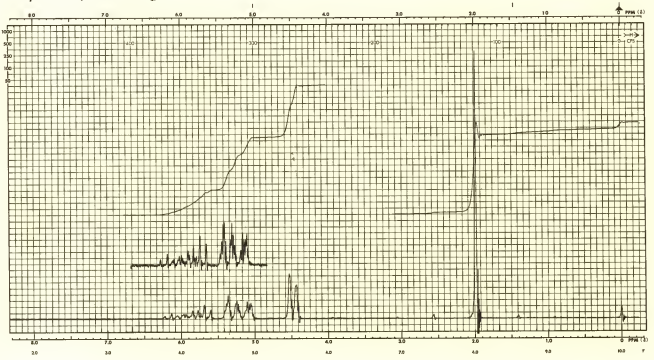
m/e	% of *P*
100 (*P*)	100.

Due to low value of parent peak impossible to determine values for $P + 1$ and $P + 2$.

Ultraviolet Data

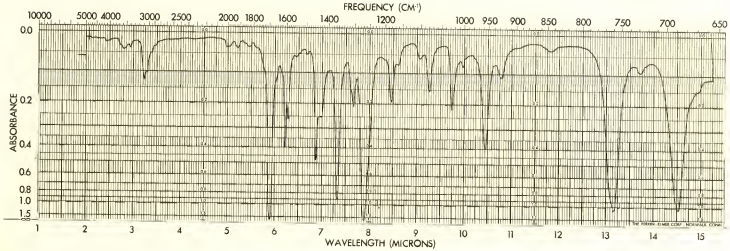
Transparent above 210 mμ.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound No. 7-4
Beilstein Ref. 7, 271



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
38	4.	74	5.
39	7.	76	3.
43	6.	77	77.
50	16.	78	9.
51	40.	105	100.
52	3.	120	24.3
61	4.	121	2.15
62	7.	122	0.15
63	11.		

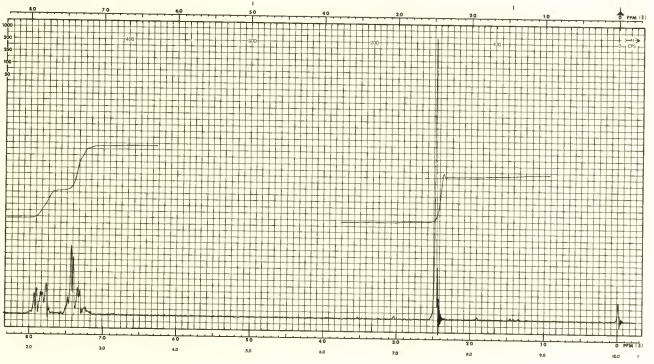
ISOTOPE ABUNDANCES

m/e	% of *P*
120 (*P*)	100.
121 (*P* + 1)	8.83
122 (*P* + 2)	0.62

Ultraviolet Data

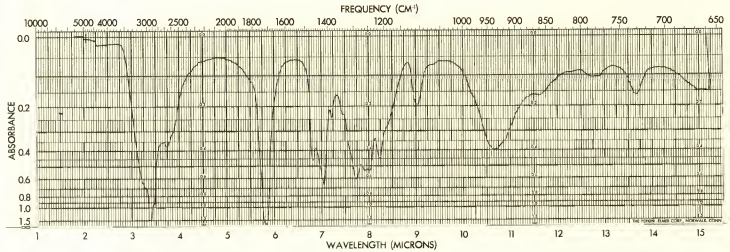
λ_{max}^{EtOH}	$\log \epsilon_{max}$
245	4.1
280	3.1
320	1.9

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound No. 7-5
Beilstein Ref. **2**, 321



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

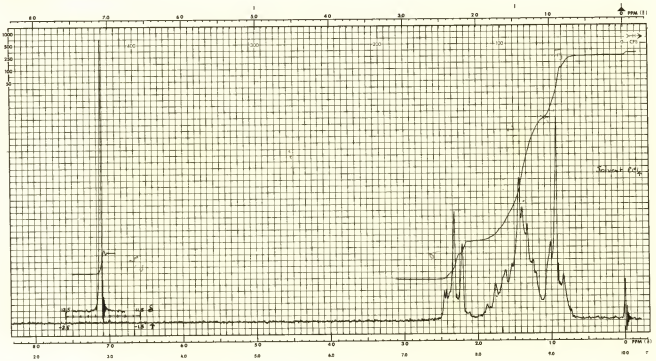
m/e	% of base peak	*m/e*	% of base peak
26	6.	57	12.
27	41.	60	100.
31	4.	61	9.
39	21.	69	4.
41	37.	70	4.
42	18.	73	45.
43	25.	74	7.
45	22.	84	12.
55	17.	116	0.02
56	9.		

The 116 peak was established as the parent peak since the ratio of the 117 to the 116 peak increased with an increase in the size of sample. $P + 1$ and $P + 2$ peaks are too small to measure accurately.

Ultraviolet Data

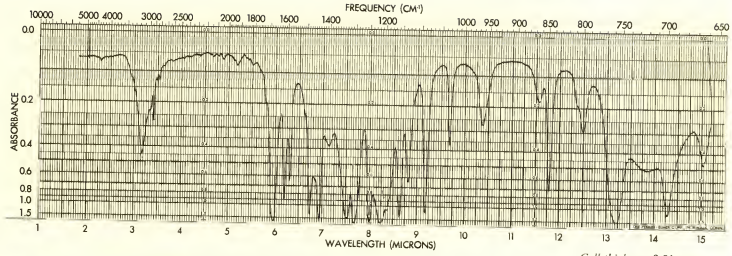
Featureless beyond 210 mμ.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound No. 7-6
*Beilstein Ref. **10**, 70*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	4.	65	34.
29	8.	66	5.
37	4.	92	83.
38	10.	93	17.
39	30.	120	100.
50	3.	121	34.
53	11.	122	3.
62	11.	152	44.99
63	23.	153	4.10
64	22.	154	0.48

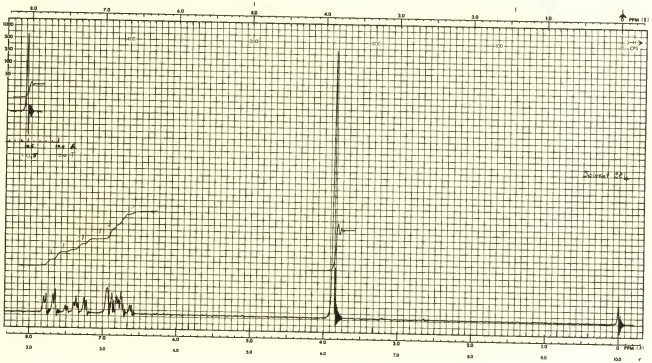
ISOTOPE ABUNDANCES

m/e	% of *P*
152 (*P*)	100.
153 (*P* + 1)	9.10
154 (*P* + 2)	0.96

Ultraviolet Data

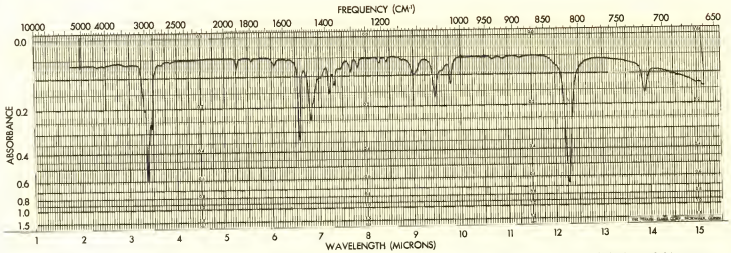
	λ_{max}^{EtOH}	log ϵ_{max}
pH 7	238	3.95
	306	3.62
pH 13	247	3.87
	338	3.79

NMR Spectrum (*Solvent CCl_4*)



Infrared Spectrum

Compound No. 7-7
Beilstein Ref. 5, 420



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
39	8.	115	7.
41	7.	116	3.
51	4.	117	9.
63	6.	119	100.
65	8.	134	21.53
77	8.	135	2.58
91	20.	136	0.16
103	5.		
104	4.		
105	4.		

ISOTOPE ABUNDANCES

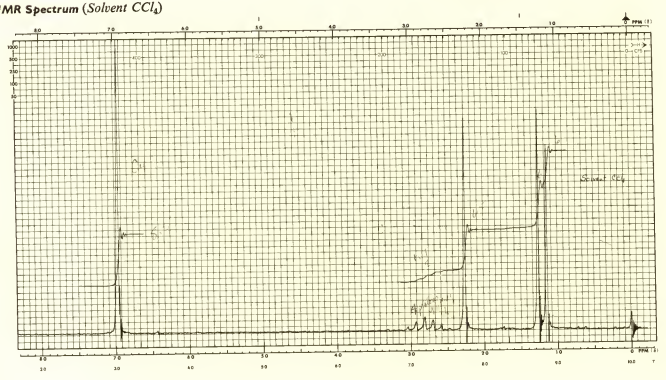
m/e	% of *P*
134 (*P*)	100.
135 (*P* + 1)	11.90
136 (*P* + 2)	0.74

Ultraviolet Data

$\lambda_{max}^{Isooctane}$	log ϵ_{max}
252 (*s*)	2.2
259	2.47
265	2.62
266 (*s*)	2.60
273	2.64

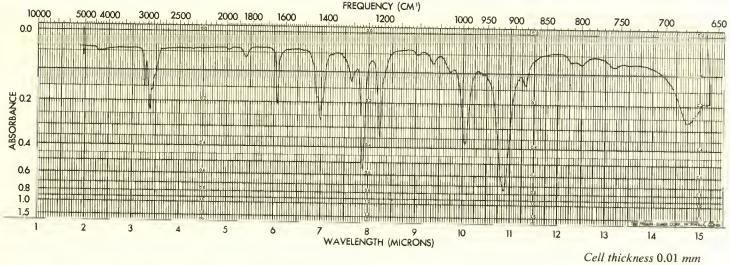
(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound No. 7-8
Beilstein Ref. 1, (111), 727



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	13.	54	10.
27	42.	55	100.
38	4.	56	5.
39	28.	57	3.
41	17.	134	4.18
50	5.	135	0.21
51	5.	136	4.24
53	10.	137	0.19

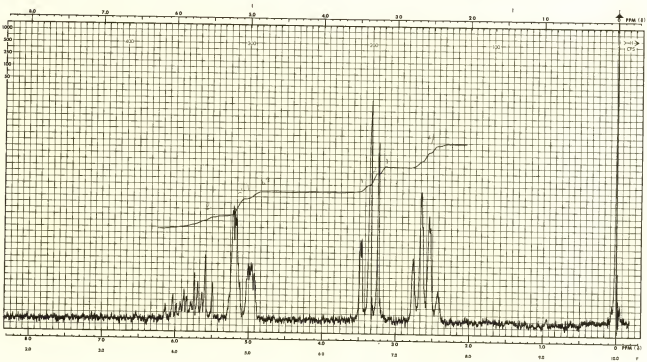
ISOTOPE ABUNDANCES

m/e	% of *P*
134 (*P*)	100.
135 (*P* + 1)	5.1
136 (*P* + 2)	101.4
137 (*P* + 3)	4.5

Ultraviolet Data

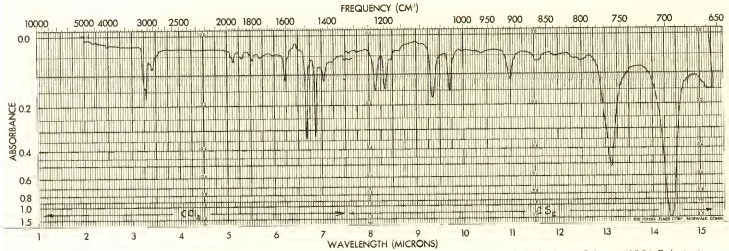
Featureless above 210 mμ.

NMR Spectrum (*Solvent CCl*$_4$)



Infrared Spectrum

Compound No. 7-9
Beilstein Ref. 6, 465



Cell thickness 0.1 *mm* (10% *Solution*)

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
28	5.	89	4.
39	13.	91	100.
41	4.	246	4.65
45	30.	247	0.79
50	3.	248	0.47
51	10.		
63	8.		
64	3.		
65	32.		
77	8.		

ISOTOPE ABUNDANCES

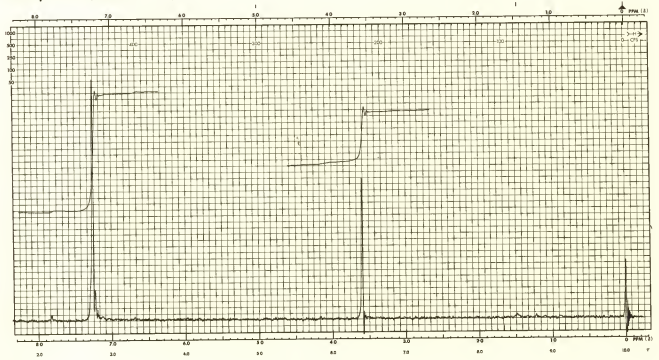
m/e	% of *P*
246 (*P*)	100.
247 (*P* + 1)	17.0
248 (*P* + 2)	10.2

Ultraviolet Data

λ_{max}^{EtOH}	$\log \epsilon_{max}$
265 (*s*)	3.1
285 (*s*)	2.4

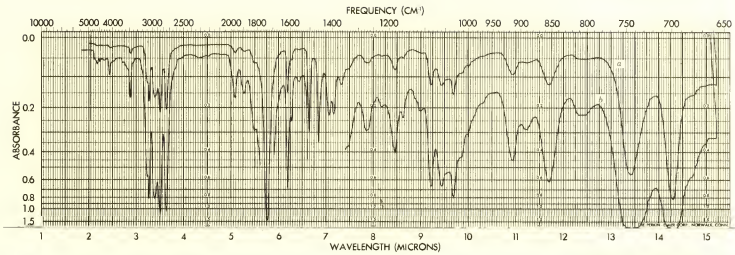
(*s*) = shoulder.

NMR Spectrum (*Solvent* $CDCl_3$)



Infrared Spectrum

Compound No. 7-10
Beilstein Ref. 7, 304



a. *Cell thickness* 0.01 *mm*
b. *Cell thickness* 0.05 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak	*m/e*	% of base peak
26	4.	62	4.	92	70.
27	18.	63	11.	93	5.
29	18.	65	18.	102	4.
38	5.	74	4.	103	16.
39	23.	75	3.	104	8.
41	4.	76	3.	105	41.
50	14.	77	30.	106	5.
51	30.	78	50.	115	6.
52	7.	79	20.	116	5.
53	4.	89	4.	133	9.
55	4.	90	3.	134	57.4
56	4.	91	100.	135	5.80
				136	0.41

ISOTOPE ABUNDANCES

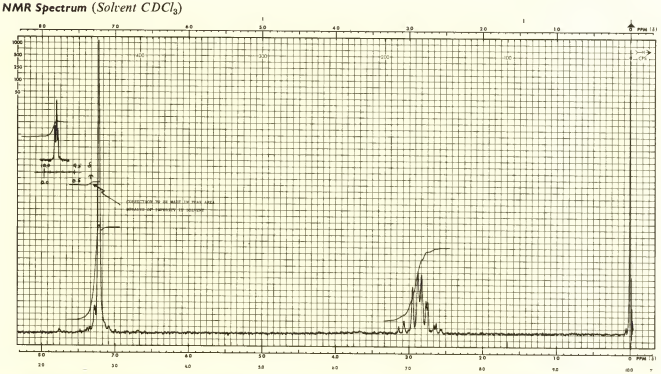
m/e	% of *P*
134 (*P*)	100.
135 (*P* + 1)	10.1
136 (*P* + 2)	0.71

Ultraviolet Data

$\lambda_{max}^{n.s.g.}$	log ϵ_{max}
249	2.31
253	2.50
255	2.50
259	2.47
262	2.43
264	2.18
268	2.25
283	1.59

n.s.g. = no solvent given.

NMR Spectrum (*Solvent* $CDCl_3$)

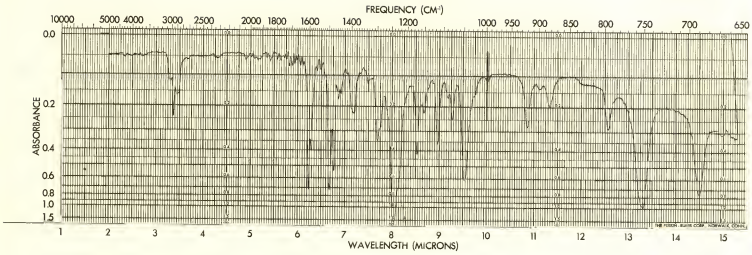


CHAPTER EIGHT

Sets of Spectra, Unidentified

This chapter consists of ten sets of spectra. These are presented without identification or reference.

Infrared Spectrum *Compound 8-1*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	4.	66	18.
27	14.	77	10.
29	10.	94	100.
38	5.	95	7.
39	22.	122	35.3
50	5.	123	3.12
51	10.	124	0.23
55	3.		
63	5.		
65	14.		

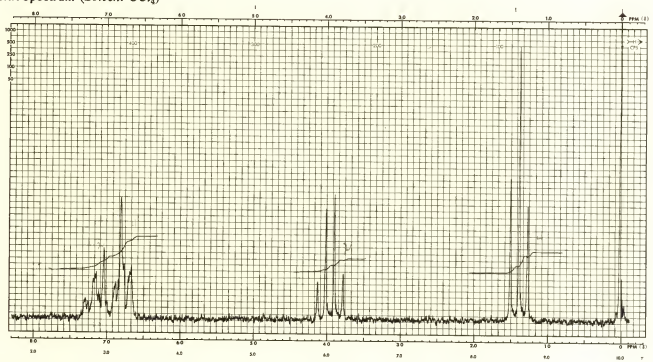
ISOTOPE ABUNDANCES

m/e	% of *P*
122 (*P*)	100.
123 (*P* + 1)	8.86
124 (*P* + 2)	0.66

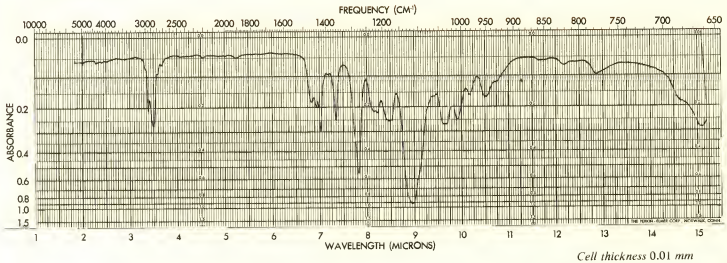
Ultraviolet Data

$\lambda_{max}^{Isooctane}$	log ϵ_{max}
222	3.88
254	3.12
260	3.28
267	3.25

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum *Compound 8-2*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	14.	95	13.
27	100.	107	3.
28	20.	108	87.
29	17.	109	4.
31	8.	110	74.
42	5.	138	95.
43	16.	139	3.
80	3.	140	90.
81	6.	141	3.
93	14.	150	3.
94	4.	230	1.10
		232	2.12
		234	1.06

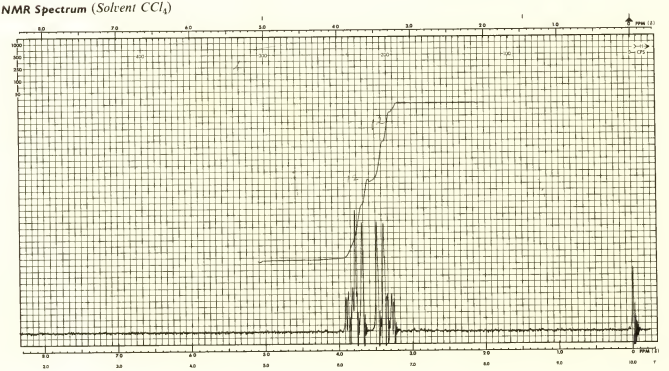
ISOTOPE ABUNDANCES

m/e	% of *P*
230 (*P*)	100.
232 (*P* + 2)	194.2
234 (*P* + 4)	95.7

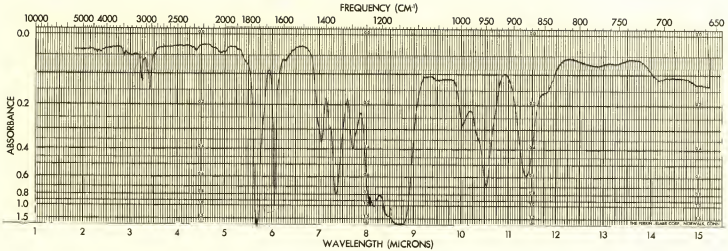
Ultraviolet Data

λ_{max}^{EtOH}	ϵ_{max}
305 (inflection)	1.5

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum *Compound 8-3*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak	*m/e*	% of base peak
25	7.	47	6.	88	18.
26	25.	55	100.	89	10.
27	82.	56	6.	99	7.
28	41.	57	3.	103	7.
29	67.	58	12.	115	3.
32	9.	59	15.	117	8.
34	6.	60	27.	131	16.
40	5.	61	15.	143	24.
42	29.	70	4.	159	4.
43	44.	71	3.	187	12.
44	48.	73	6.	230	3.30
45	31.	75	5.	231	0.40
46	18.	87	4.	232	0.18

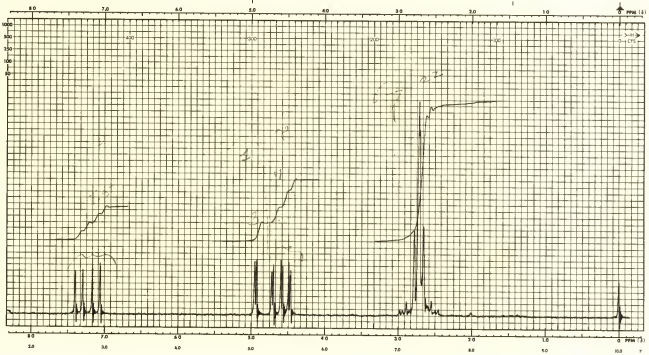
ISOTOPE ABUNDANCES

m/e	% of *P*
230 (*P*)	100.
231 (*P* + 1)	12.0
232 (*P* + 2)	5.4

Ultraviolet Data

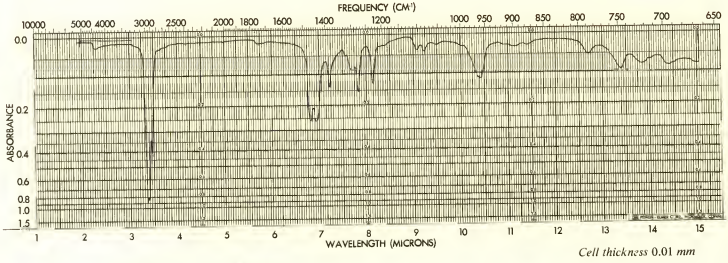
Featureless above 210 mμ.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum

Compound 8-4



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	6.	55	11.
27	40.	56	62.
28	10.	57	14.
29	30.	61	100.
35	10.	62	13.
39	16.	63	5.
41	48.	75	18.
45	23.	89	5.
46	13.	104	53.3
47	27.	105	3.7
48	25.	106	2.6
49	35.		

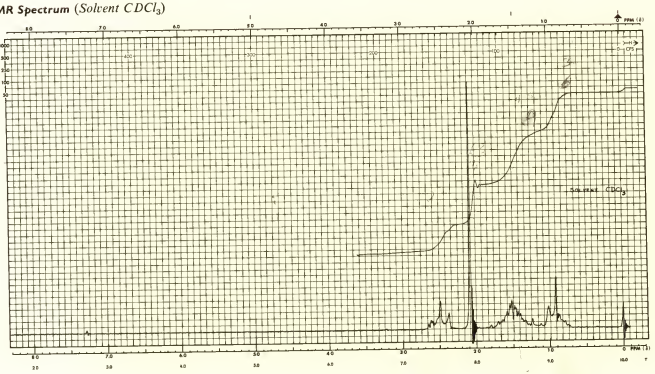
ISOTOPE ABUNDANCES

m/e	% of *P*
104 (*P*)	100.
105 (*P* + 1)	6.45
106 (*P* + 2)	4.77

Ultraviolet Data

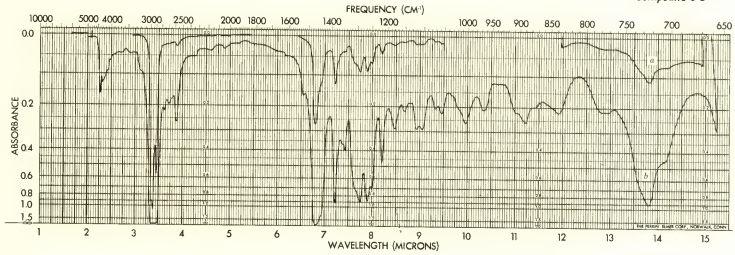
λ_{max}^{EtOH}	ϵ_{max}
228 (inflection)	106

NMR Spectrum (*Solvent* $CDCl_3$)



Infrared Spectrum

Compound 8-5



a. *Cell thickness* 0.01 *mm* b. *Cell thickness* 0.1 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	5.	53	4.
27	49.	54	4.
28	10.	55	45.
29	31.	56	100.
35	5.	57	9.
39	25.	59	4.
40	4.	60	4.
41	57.	61	16.
42	39.	69	26.
43	58.	84	16.
45	13.	89	4.
46	6.	118	30.2
47	31.	119	2.40
		120	1.50

ISOTOPE ABUNDANCES

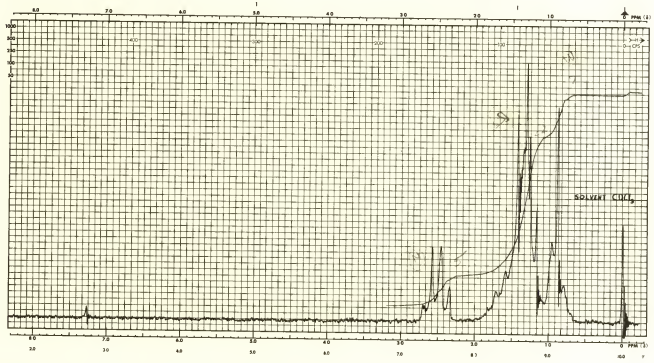
m/e	% of *P*
118 (*P*)	100.
119 (*P* + 1)	7.95
120 (*P* + 2)	4.96

Ultraviolet Data

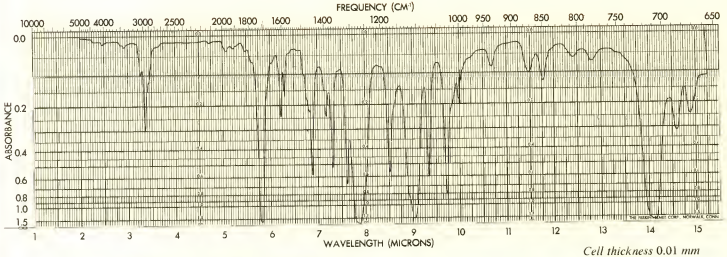
$\lambda^{C_6H_{12}}_{max}$	ϵ_{max}
225 (*s*)	163

(*s*) = shoulder.

NMR Spectrum (*Solvent* $CDCl_3$)



Infrared Spectrum — **Compound 8-6**



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	3.	77	52.
27	13.	78	6.
29	10.	105	100.
50	12.	106	11.
51	29.	122	30.
74	3.	150	16.28
76	4.	151	1.72
		152	0.14

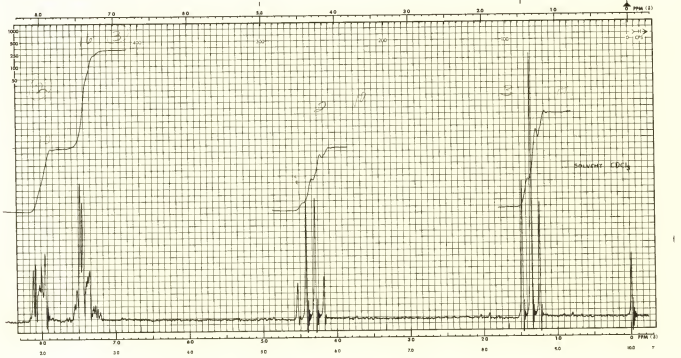
ISOTOPE ABUNDANCES

m/e	% of *P*
150 (*P*)	100.
151 (*P* + 1)	10.2
152 (*P* + 2)	0.88

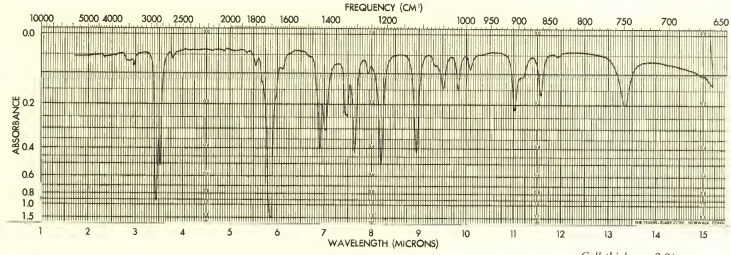
Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
229	4.08
272	2.90
280	2.85

NMR Spectrum (*Solvent* $CDCl_3$)



Infrared Spectrum *Compound 8-7*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	8.	51	4.
27	34.	53	5.
28	14.	54	7.
29	9.	55	100.
38	4.	56	11.
39	25.	69	24.
40	7.	70	21.
41	31.	80	4.
42	71.	83	7.
43	10.	98	32.80
50	4.	99	2.30
		100	0.16

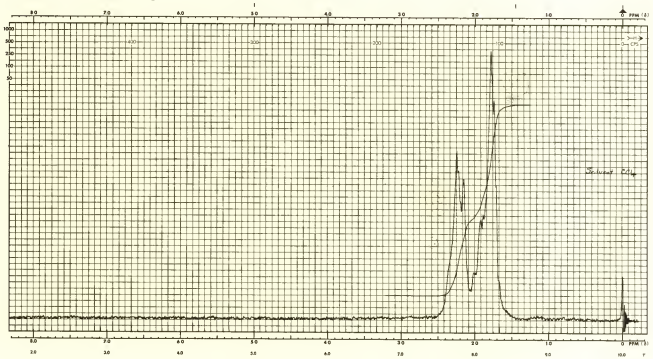
ISOTOPE ABUNDANCES

m/e	% of *P*
98 (*P*)	100.
99 (*P* + 1)	7.00
100 (*P* + 2)	0.47

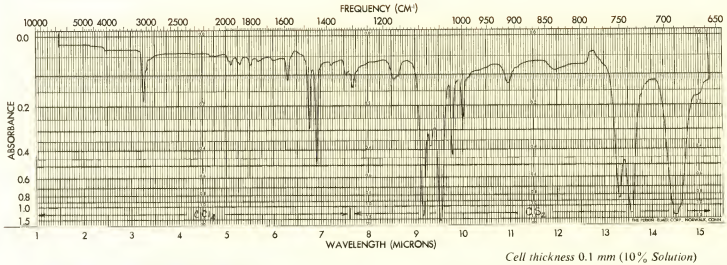
Ultraviolet Data

λ_{max}^{EtOH}	log ϵ_{max}
285	1.2

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum *Compound 8-8*



Cell thickness 0.1 *mm* (10% *Solution*)

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak	*m/e*	% of base peak
27	8.	75	5.	141	9.
28	32.	76	4.	147	5.
32	6.	77	52.	152	8.
39	16.	78	11.	153	11.
44	4.	92	5.	154	64.
45	8.	93	9.	155	8.
50	23.	96	4.	173	15.
51	5.	97	33.	174	8.
52	5.	108	4.	184	12.
53	4.	109	6.	185	14.
63	5.	110	8.	186	11.
65	39.	111	4.	202	100.
69	9.	122	4.	203	13.5
74	6.	125	13.	204	5.1

ISOTOPE ABUNDANCES

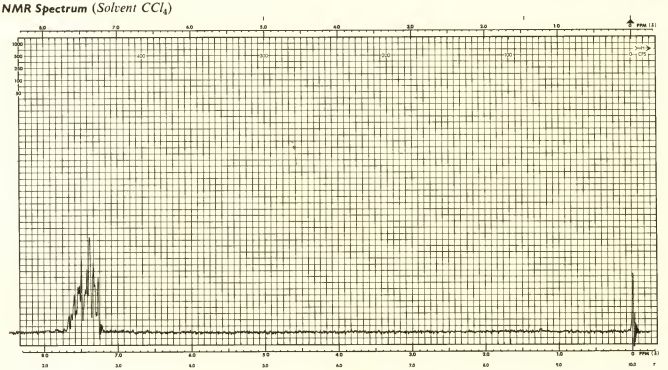
m/e	% of *P*
202 (*P*)	100.
203 (*P* + 1)	13.5
204 (*P* + 2)	5.1

Ultraviolet Data

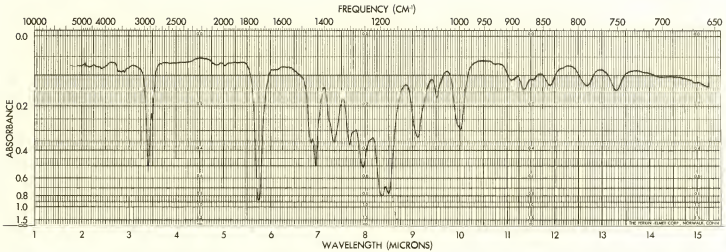
λ_{max}^{EtOH}	$\log \epsilon_{max}$
232	4.15
262 (*s*)	3.38

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum *Compound 8-9*



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
26	7.	45	5.
27	45.	55	9.
29	17.	59	25.
31	6.	71	53.
38	4.	74	66.
39	22.	87	17.
41	36.	102	1.2
42	20.	103	0.084
43	100.	104	0.011
44	5.		

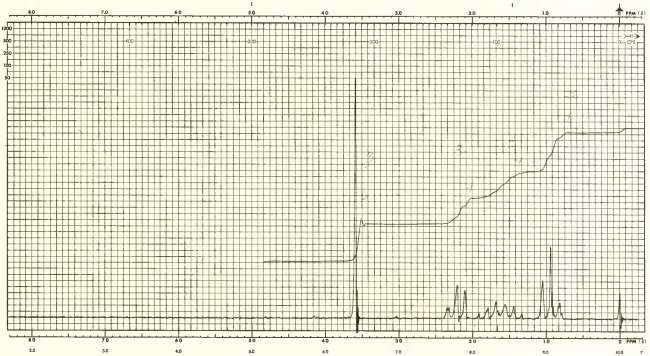
ISOTOPE ABUNDANCES

m/e	% of *P*
102 (*P*)	100.
103 (*P* + 1)	7.36
104 (*P* + 2)	0.9

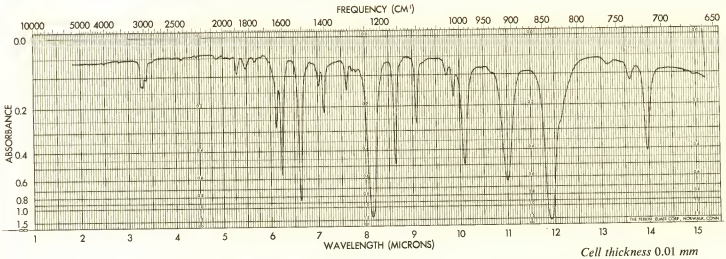
Ultraviolet Data

Transparent above 210 mμ.

NMR Spectrum (*Solvent* CCl_4)



Infrared Spectrum — Compound 8-10



Cell thickness 0.01 *mm*

Mass Spectral Data (Relative Intensities)

m/e	% of base peak	*m/e*	% of base peak
27	5.	70	5.
31	4.	75	14.
39	6.	94	4.
50	11.	95	6.
51	13.	96	30.
57	5.	101	26.
60	4.	102	5.
61	6.	121	33.
62	3.	122	100.
63	5.	123	8.88
69	4.	124	0.52

ISOTOPE ABUNDANCES

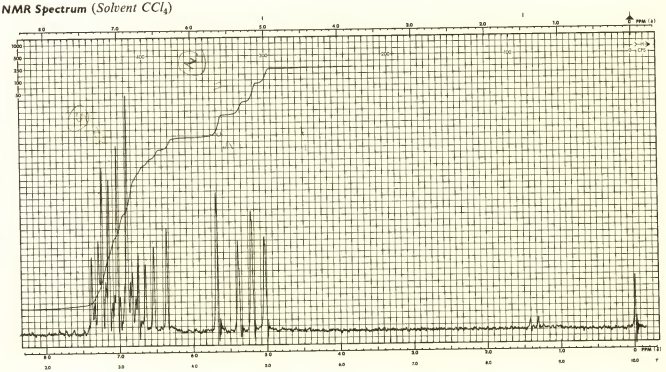
m/e	% of *P*
122 (*P*)	100.
123 (*P* + 1)	8.88
124 (*P* + 2)	0.52

Ultraviolet Data

λ_{max}^{EtOH}	$\log \epsilon_{max}$
245	4.10
256 (*s*)	3.88
277	2.91
283	2.92
293	2.74

(*s*) = shoulder.

NMR Spectrum (*Solvent* CCl_4)



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Key: MS = Mass spectrometry
IR = Infrared spectrometry
NMR = Nuclear magnetic resonance spectrometry
UV = Ultraviolet spectrometry